

THE DIRECT LIQUEFACTION PROOF OF CONCEPT PROGRAM

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INTRODUCTION: - Demonstration Operations at the Direct Liquefaction Proof-Of-Concept Facility at the HRI Research and Development Center in Lawrenceville, N.J. are funded by the U.S. Department of Energy, Hydrocarbon Research Inc. and the Kerr-McGee Corporation. The facility is operated and managed by Hydrocarbon Research Inc.

The Proof of Concept Facility consists of several distinct process units, a Coal Handling System, a Slurry Preparation-Pumping-Preheating System, Two Ebulated-Bed Reactors in Series, an On-Line Hydrotreater, Separation and Pressure Let-Down System, Scrubbing and Oil-Water Separation, Flash Vessels and Atmospheric and Vacuum Distillation Equipment, a Rose-SRSM and U.S. Filter Solid Liquid Separation Systems and Product Storage. The POC Process Development Unit (PDU) processes about 3 tons a day of coal producing about 15 barrels per day of clean distillate liquid product and can operate with or without solids containing recycle solvent. The Rose-SR unit and On-Line Hydrotreater were added along with other improvements to the equipment and control systems prior to the CTSLTM Process Scale-Up with Illinois #6 Bituminous Coal. *Figure 1* shows a schematic of the process.

The Catalytic Two Stage Liquefaction Process (CTSL) is an advanced direct coal liquefaction process that utilizes a low temperature first stage to foster hydrogenation in the presence of a nickel molybdenum ebullated bed catalyst and a higher temperature second stage to increase conversion and heteroatom removal. In POC Run 01, the main objective was to scale-up the CTSL Process with Illinois #6 coal in the extinction recycle mode to produce an all distillate slate of products.

The Proof of Concept Program started in October 1992 with the first year devoted to a facility upgrade, followed by operations on POC Run 01 through February 1994.

PROGRAM AND POC-01 OBJECTIVES - The overall program objective is to develop direct coal liquefaction and associated transitional technologies which are capable of producing premium liquid fuels, which are competitive with petroleum and which can be produced in an environmentally acceptable manner.

POC-1 objectives were to confirm equipment operability, to collect data in the CTSL mode of operation while feeding Illinois #6 Crown II Mine coal, to collect 2500 gallons of distillate for upgrading studies, to evaluate the ROSE-SRSM and U.S. Filter Systems, and to provide a comparison with the existing data base.

FACILITY UPGRADE - During the first year the POC facility was modified to improve reliability and to provide the flexibility to operate in several alternate modes. Kerr-McGee's Rose-SRSM unit from Wilsonville, Alabama was redesigned and installed at HRI to allow a comparison with the U.S. Filter solids separation system. Also included was modifying a reactor from Wilsonville, enlarging the reactor structure, installing an on-line hydrotreater, providing interstage sampling, upgrading the computer control and data acquisition system, revising the preheaters and connecting to an alternate power supply grid.

OPERATIONS - Run POC-1 started on October 29, 1993 feeding Illinois #6 coal using 1/16th inch Ni-Mo on alumina catalyst in each of two ebullated reactors and with hydrogenated Cat Cycle oil for start-up. The operating conditions plan as shown in the following Operating Summary consisted of five main conditions with some variations in conditions 3 & 4, (See Table 1). As indicated the space velocity and reaction temperatures were increased and the solvent/coal ratio was decreased as the run progressed. In addition

the catalyst addition rate was increased as planned and inadvertently decreased by mal-operation of the catalyst addition system in periods 47-58. Fifty-eight days on coal feed were completed concluding in a planned shutdown in February 1994.

RESULTS & ACCOMPLISHMENTS - This run was a successful scale-up of the CTSL processing of Illinois #6 coal with a Rose-SR solid separation unit. In the first two operating conditions at moderate temperatures and at low space velocity (2 tons/day), high distillate yields and conversion were observed; C4-975F yields of 73-82% of MAF coal and 975F+ Conversions of 86-95%. These results confirmed bench scale data and as seen in *Table 2* were sustained in ensuing periods despite variations in Deasher performance as optimum operating conditions and procedures were being developed. In the latter stages of the operation, resid conversion and distillate yield decreased due to problems with the catalyst addition system and low resid recovery from the Rose-SR Deasher due to a 10% increase in asphaltene yield. The downward trends of key performance indicators as the run progressed are depicted in Figure 2.

Some of the major accomplishments of this initial run are:

- Successfully operated a new 3 ton/day two stage ebullated-bed reactor system incorporating a Rose-SR solid separation unit.
- Demonstrated distillate production at C4-975F levels of 70-75wt% MAF and coal conversions of 94-96% with Illinois #6 coal.
- Achieved a Bottoms Energy Rejection of 12% for a sustained period of Rose-SR operation. Retrograde reactions were not observed.
- Achieved operation with a more concentrated feed slurry; coal concentrations up to 53%.
- Collected 3500 Gallons of 150-650F distillate (0.06% N, 0.03% S) for upgrading and engine testing.
- Evaluated various materials of construction in a high temperature hydrogen environment.

Plans - Run POC-2 is starting in May of this year. It is scheduled to be a 40 day operation on sub-bituminous Black Thunder Mine Wyoming coal investigating scale-up of the CTSL Process with on-line hydrotreating, Rose-SR and Filtration Separation and most importantly whether or not solid deposition occurs in the process equipment and lines. POC-3 is scheduled for October 1994 and will study the co-processing of sub-bituminous coal and a high metals, California Petroleum Resid over a 40 day period. POC-4 is planned for early 1995 with the objective to study the scale-up of the processing of sub-bituminous coal using dispersed and supported catalysts.

Acknowledgement

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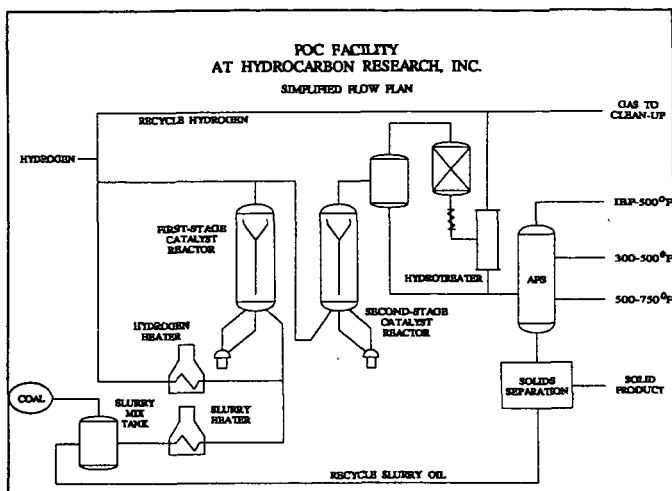


Figure 1

| POC-01 Operating Summary Illinois No. 6 Crown II Mine Coal Akzo AO-60 1/16" Extrudate Catalysts | | | | | | | |
|--|------------|------------|------------|--------------|----------------|-------------|---------|
| Condition Period No | 1 13-19 | 2 20-26 | 3 27-32 | 3B 41-44A | 4 A/B 47-50 | 4C 54-57 | 5 58 |
| Recycle Mode | Ashy | Solid-Free | | | | | |
| Space Velocity [lb ml coal/hr ft ³ reactor] | 19 | 20 | 29 | 29 | 27 | 29 | 28 |
| Solvent/Coal Ratio | 1.2 | 1.25 | 1.26 | 1.39 | 1.4 | 1.0 | 1.1 |
| First Stage | | | | | | | |
| Temp F | 768 | 765 | 775 | 770 | 775 | 775 | 775 |
| Cat. Repl. Rate [lb/ton ml coal] | 0.5 | 1.5 | 1.5 | 1.5 | 0 | 0 | 0 |
| Second Stage | | | | | | | |
| Temp [F] | 799 | 810 | 815 | 810 | 812 | 820 | 824 |
| Cat. Repl. Rate [lb/ton ml coal] | 1.0 | 3.0 | 3.0 | 3.0 | 3.0 | 0 | 0 |

TABLE 1

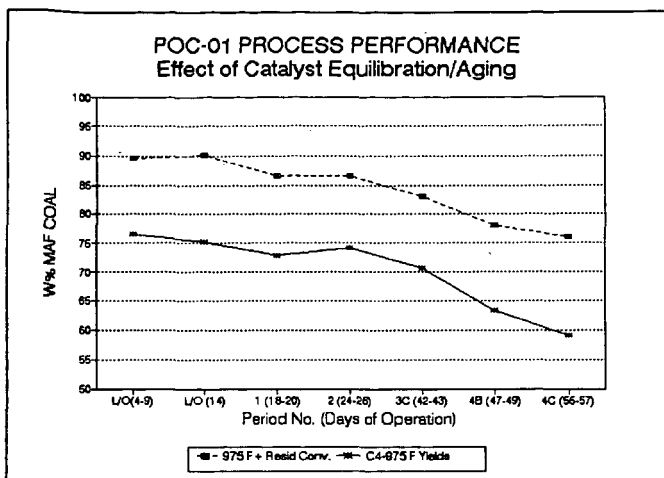


Figure 2

| POC-01 PROCESS PERFORMANCE | | | | | | |
|---|-------------------|------------|------------|-------------|-------------|-------------|
| Coal: Illinois No. 6 Crown II Mine (10.4 w% Dry Ash) | | | | | | |
| Catalyst: Akzo AO-60 1/16" NiMo Extrudates in both Reactors | | | | | | |
| Process Conditions Periods | L/O Rose-SR 14 | 1 18-20 | 2 24-26 | 3B 42-43 | 4B 47-49 | 4C 55-57 |
| Recycle Type | Ashy | Ashy | Ash-free | | | |
| Reactor K-1: Temperature, Deg. C | 409 | 408 | 407 | 411 | 414 | 413 |
| Reactor K-2: Temperature, Deg. C | 426 | 432 | 432 | 433 | 433 | 436 |
| Flow Rates Coal Feed, Kg/hr | 68.6 | 69.5 | 70.2 | 87.9 | 89.8 | 102.8 |
| Process Performance | | | | | | |
| Chemical H ₂ Consumption, W% MAF | 7.6 | 7.1 | 7.1 | 6.1 | 5.9 | 5.3 |
| Coal Conversion, W% MAF | 95.2 | 95.6 | 95.0 | 94.7 | 95.1 | 95.4 |
| 524 C+ Conversion, W% MAF | 90.1 | 86.6 | 86.6 | 83.0 | 78.0 | 76.0 |
| Desulfurization (Organic), W% | 98.3 | 98.0 | 97.7 | 96.0 | 94.4 | 94.0 |
| Denitrogenation, W% | 88.2 | 86.0 | 82.5 | 78.2 | 75.9 | 78.0 |
| C4-524 C Distillates, W% MAF | 75.1 | 72.8 | 74.2 | 70.64 | 63.2 | 58.8 |
| Deasher Performance | | | | | | |
| Deasher | Vacuum Still | ROSE-SR | | | | |
| Energy Rejection, % | 23.1 | 25.2 | 16.5 | 12.8 | 22.5 | 33.0 |
| Deasher Coal Conversion, W% MAF | 94.8 | 95.7 | 95.1 | 95.2 | 95.2 | 94.9 |

TABLE 2

LIQUEFACTION OF BLACK THUNDER COAL WITH COUNTERFLOW REACTOR TECHNOLOGY

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INTRODUCTION

There is currently a resurgence of interest in the use of carbon monoxide and water to promote the solubilization of low rank coals in liquefaction processes¹⁻³. The mechanism for the water shift gas reaction (WGSR) is well documented^{4,5} and proceeds via a formate ion intermediate at temperatures up to about 400°C. Coal solubilization is enhanced by CO/H₂O and by the solvent effect of the supercritical water. The WGSR is catalyzed by bases (alkali metal carbonates⁶, hydroxides, acetates⁷, aluminates⁸). Many inorganic salts which promote catalytic hydrogenation are rendered inactive in CO/H₂O^{6,9}, although there is positive evidence for the benefit of using pyrite for both the WGSR and as a hydrogenation catalyst¹⁰.

The temperatures at which coal solubilization occurs are insufficient to promote extensive cracking or upgrading of the solubilized coal. Therefore, a two step process might achieve these two reactions sequentially. Alberta Research Council (ARC) has developed a two-stage process for the coprocessing of low rank coals and petroleum resids/bitumens¹¹. This process was further advanced by utilizing the counterflow reactor (CFR) concept pioneered by Canadian Energy Developments (CED) and ARC. The technology is currently being applied to coal liquefaction. The two-stage process employs CO/H₂O at relatively mild temperature and pressure to solubilize the coal, followed by a more severe hydrocracking step. The counterflow reactor offers several advantages over co-current operations including: separation of the gas and light oil components, thus permitted a reduction in size of the reactors; concentration of the heavier components in the liquid phase such that their time spent in the reactors exceeds the nominal residence time; concentration of the active catalyst in the liquid phase; removal of the light components in the gas phase, resulting in less secondary cracking to gas. This paper describes the results of an autoclave study conducted to support a bench unit program on the direct liquefaction of coals.

EXPERIMENTAL

The procedure for the operation of the stirred autoclave (1 litre) has been described elsewhere³. Briefly coal (80g), solvent (120g), catalyst and water were charged into the autoclave. Carbon monoxide (400-800 psi) or hydrogen (1000 psi) was introduced, resulting in a typical operating pressure of 2500 ± 300 psi, depending on temperature and extent of the WGS reaction. The produced gas was discharged at ~150°C and collected. The autoclave flushed with a nitrogen purge (75L). Both gas samples were quantified by gas chromatography. Liquid products were transferred from the autoclave by addition of toluene at > 60°C (see later). Water, removed in the gas stream, was recovered by Dean-Stark extraction, at the same time toluene soluble oils (including asphaltenes) were extracted. The solid residue was further extracted with tetrahydrofuran (THF). The insoluble organic matter was determined following a proximate analysis. Asphaltenes were measured on an aliquot of the toluene soluble oils following removal of the toluene by a rotary evaporator. Attempts were made to distill the soluble oils. This procedure (D1160) proved ineffective, largely because of the solvent cut off point (about 450°C) which resulted in a poor reproducibility since there was little product in the 450-525°C range.

The solvent was obtained from Wilsonville, run number 263. Five barrels of V-1074 oils were received. These oils were sufficiently different in properties that a blend was prepared containing 20% from each barrel. The oils were extremely waxy and did not flow until 55-60°C. Black Thunder coal was provided by Thunder Basin Coal Company. It was partially dried prior to use to facilitate crushing and pulverization.

RESULTS and DISCUSSION

Solvent Stability

The solvent (V-1074 blend) had been produced from a hydrocracking process at Wilsonville and was partially hydrogenated (H/C mole ratio 1.16). Although listed as nominally boiling within the gas oil range, a crude simulated distillation found 14.2% of 525+ resid. A D1160 distillation of a similar material (Wilsonville Run 262) reported 95% of distillable by 501°C. Despite the apparent small amount of resid the V-1074 blend had 12.0% pentane insoluble asphaltenes.

Under standard 1st stage conditions (390°C/600 psi CO/30 minutes), Run 49, the solvent distillation range was virtually unchanged and gas yield was barely detectable (Table 1). At the highest temperature tested for 1st stage operation 410°C, gas yield was still below 1% and light oil distribution was stable. It took operation at 2nd stage conditions before a substantial change in solvent properties occurred, then decomposition to lighter oils and gas was evident. Throughout the range of conditions the asphaltene content remained almost constant suggesting that regressive reactions were not likely to present a problem in bench unit operations. Introduction of coal however might alter this observation. When 5% coal was introduced into the feed, asphaltenes increased from 12 to 19% under two-stage conditions.

Stoichiometry of the WGSR

The stoichiometry of the WGSR is complicated by the production CO and CO₂ from the coal, the presence of the K₂CO₃ catalyst and the reaction of hydrogen with the coal/solvent. In tests with this catalyst, the CO₂ produced exceeded the stoichiometric quantity from the CO consumption in the WGSR. Typically from 0.2-0.35 moles of excess CO₂ was found with a variety of catalysts or in the absence of catalyst (Table 2), which eliminated K₂CO₃ as the source. The water recovered was also between 0.2 and 0.30 moles less than predicted by the WGSR. In the absence of catalyst (Run 55) CO was actually produced, therefore it appeared that missing water could have reacted with CO from the coal to give CO₂. If this explanation is valid, then hydrogen consumption, defined as the difference between CO reacted and hydrogen produced, was greater than values previously reported³. This would not add to the economics of the process since this addition of hydrogen was derived from the coal and water, not from introduced CO.

Catalyst Activity

Literature reports agree that potassium carbonate is amongst the most effective WGSR catalysts. This work confirmed that K₂CO₃ out performed the other tested catalysts in terms of CO conversion, however this did not correlate with coal conversion (Table 2). When using FeS, Fe₂O₃/CS₂, K₂CO₃ or NaAlO₂, the coal conversions were all similar at 80-82% (repeat runs with K₂CO₃ gave a standard deviation of ±3%), yet the CO conversion ranged from 6-80%. Surprisingly the only runs which gave poorer coal conversion, were those using the molybdenum salts, ammonium molybdate (AM) and ammonium tetrathiomolybdate (ATM) or no catalyst. Apart from potassium carbonate, only the aluminate gave substantial CO conversion.

Petrographic examination of the residues gave some insight into the liquefaction process. With K₂CO₃ the vitroplast was almost completely solubilized, and what was left (2.7%) appeared little changed from the original coal. At the other extreme, i.e. without catalyst, there was no vitroplast present. Here the majority of the coal fragments were rounded cenospheres and vacuoles (72%), as is often seen with coal pyrolysis residues. Iron sulphide catalyst duplicated the results seen without catalyst (i.e. 66% cenospheres and vacuoles). In both cases only 9% CO conversion was recorded. NaAlO₂ was intermediate between these extremes for both CO conversion and residue appearance. A small portion of the coal remained as vitroplast (5%) while some vacuoles were formed (4%). The devolatilization process could ultimately lead to the formation of char. The presence of CO, when it underwent the WGSR, appeared to suppress this pathway to char. A high concentration of CO was required since vacuoles were also observed with syngas or CO/nitrogen atmospheres.

Liquefaction product yields were measured as asphaltenes, preasphaltenes and hydrocarbon gases (Table 3). The remaining products, including pentane soluble oils, carbon oxides and produced water, were grouped together as oils+, since their quantification was less reliable. Oils+ were, therefore, set numerically to the difference between the coal conversion and the sum of asphaltenes, preasphaltenes and hydrocarbon gases. This technique eliminated the need for corrections for mass balance, losses of light components during rotary evaporation of the toluene solubles, and changes in solvent composition during the run. Hydrocarbon gas yields at 390°C/30 minutes were consistent at 1.3-1.5g/100g MAF coal, irrespective of the catalyst employed. These values were independent of the coal conversion or the distribution of the distillable and non-distillable oils. Only a small portion of this gas could be attributed to solvent decomposition. The remainder was from thermal decomposition of the coal.

With the benchmark catalyst (K₂CO₃) the majority of the products were asphaltenes and preasphaltenes. The remaining catalysts (ATM, Fe₂O₃, AM) performed less favourably, yielding less oils+ or less total product. ATM did show increased activity in terms of the improved ratios of asphaltenes: preasphaltenes and oils+: preasphaltenes. This activity was confirmed when K₂CO₃ and ATM were combined which resulted in much lighter product slate (increased oils+, reduced asphaltenes and preasphaltenes) at similar coal conversion. This was one combination which was subsequently selected for the bench unit program.

Process Severity

Earlier work² had identified the minimum and preferred conditions for the solubilization of Black Thunder coal, but no work had been performed on the product yield distribution. Coal and CO conversion both increased with severity there was a noticeable progression from preasphaltenes → asphaltenes → oils+ with the K_2CO_3 catalyst (Table 3, Figure 1). This contrasted with the aluminate catalyst (410°C/30 min.) which had a sharp increase in asphaltenes (410°C/30 min.) at the expense of oils+. Here solvent must have participated in regressive reactions to generate the additional asphaltenes. However the regressive reactions did not progress to preasphaltenes since little difference was seen between the K_2CO_3 and aluminate.

Simulated 2 stage tests were also performed. The test followed the standard procedure except that at the completion of the first stage the temperature was reduced to about 300°C, the CO gas was discharged and replaced with hydrogen. The temperature was raised to its new set point and the procedure continued. As anticipated there was a dramatic increase in process performance. Coal conversion rose to 91-95%. Preasphaltenes dropped to below 5% with FeS catalyst and almost zero with the molybdenum catalyst. Much of the asphaltene was also converted to oils+, especially with molybdenum where only a quarter of the products remained as asphaltenes or preasphaltenes. Gas production in the second stage was nominally 10-12g/100g coal, however much of this could be attributed to solvent breakdown.

Bench Unit Program

Much of the autoclave work was performed with potassium carbonate, as catalyst. Unfortunately this proved to be a poor practical choice because of the operational problems that arose due to its hygroscopic nature. Inevitably the bench unit lines or valves plugged with solid potassium carbonate both when it was introduced as an aqueous solution or as a fine powder in the coal/solvent slurry. Ultimately it was replaced by the sodium aluminate, which showed no tendencies to deposit or plug the narrower parts of the Bench Unit.

Coal solubilization and CO conversion in the bench unit were below the level achieved in the autoclave at nominally similar process severity for single stage operation (Figure 2). It was not possible to directly compare CO conversion in the 2 operations for a variety of reasons e.g. gas residence time, CO:coal ratio and CO/H₂O mixing and contact were not the same. However, it can be seen that the trends observed in the autoclave were paralleled by the bench unit. Coal conversion approached 80% in the best runs when the temperature was raised to 410°C, but was consistently about 10% less than the corresponding autoclave runs. This did not have a negative impact on the overall performance in the 2 stage operation as long as a shift catalyst was present. In the absence of a shift catalyst overall coal conversion was only 73% (Figure 3) for a 2 stage bench unit test at 440°C. Most of the product was asphaltenes, with less than 10% oils. When sodium aluminate was present overall conversion reached the maximum for coal conversion 92-94%. Under these conditions the product was primarily pentane soluble oils, with molybdate as usual better than iron based catalyst. Oil yield exceeded that found in the autoclave, but this technique again illustrated the trends i.e., yield structure improved with process severity up to 440°C (2nd stage) and molybdate > iron catalysts. Therefore, the autoclave was a useful predictor of process performance.

The current bench unit is a once through operation. It is anticipated that further conversion of the asphaltenes to oils could be accomplished with recycle. Preliminary autoclave tests have confirmed that the bottoms product from the counterflow reactor (including ash, catalyst and IOM) can be upgraded to lighter products.

CONCLUSIONS

An effective shift catalyst is required to process Black Thunder coal. Once through counterflow reactor processing can yield greater than 60% pentane soluble oils. Autoclave tests can predict processing trends in the bench unit counterflow reactor.

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Table 1 : Solvent Stability Tests

| | Solvent | 1st stage | 1st stage | 2 stage |
|------------------------|-------------|--------------------------------|---------------------------------------|----------------|
| Conditions* | As received | 410/600/30 | 390/600/30 | 440/1100/60 |
| Catalyst | | K ₂ CO ₃ | K ₂ CO ₃ /ATM** | FeS |
| CO conversion, % | | 57 | 66 | H ₂ |
| Gas yield,g/100g | | 0.8 | 0.1 | 2.5 |
| Simulated Distillation | | | | |
| IBP oC | 297 | 153 | 176 | 138 |
| IBP - 182oC | 0.0 | 1.5 | 1.0 | 2.8 |
| 182 - 343oC | 4.0 | 3.5 | 3.1 | 11.4 |
| 343+ oC | 96.0 | 95.0 | 95.9 | 86.8 |

* temperature, oC; initial pressure, psi; time, minutes ** Ammonium tetrathiomolybdate

Table 2 : Water Gas Shift Reaction

| Run # | * Catalyst | CO | H ₂ O | ---> | CO ₂ | H ₂ | Coal conv |
|--------|--|-------|------------------|------|-----------------|----------------|-----------|
| | | Moles | Moles | | Moles | Moles | % |
| 28 in | K ₂ CO ₃ | 1.23 | 1.88 | ---> | 0 | 0 | 88 |
| change | | -0.96 | -1.06 | | +1.19 | +0.53 | |
| 31 in | K ₂ CO ₃ /N ₂ | 0 | 1.87 | ---> | 0 | 0 | 50 |
| change | | 0 | -0.16 | | +0.20 | 0 | |
| 54 in | None | 0 | 0.53 | ---> | 0 | 1.27 | 55 |
| change | | +0.01 | -0.03 | | +0.11 | +0.27 | |
| 55 in | None | 1.25 | 0.53 | ---> | 0 | 0 | 62 |
| change | | +0.20 | -0.20 | | +0.33 | +0.02 | |
| 27 in | NaAlO ₂ | 1.25 | 1.88 | ---> | 0 | 0 | 82 |
| change | | -0.56 | -0.78 | | +0.89 | +0.24 | |
| 26 in | FeS | 1.26 | 1.88 | ---> | 0 | 0 | 81 |
| change | | -0.09 | -0.41 | | +0.49 | +0.07 | |
| 36 in | K ₂ CO ₃ | 0.85 | 1.45 | ---> | 0 | 0 | 82 |
| change | | -0.59 | -0.82 | | +0.88 | +0.24 | |

* All runs at 390oC/600psi/30mins, except Run 36 at 370oC/400psi/30mins

Table 3 : Product Yield Distribution

| Run # | Catalyst | Coal conv | CO conv | Asphalt | Preasp | Oils+ | HC gas | Severity |
|-------|---|-----------|---------|---------|--------|--------|--------|-------------|
| | | % | % | g/100g | g/100g | g/100g | g/100g | oC/psi/mins |
| 37 | K ₂ CO ₃ | 82 | 80 | 45.5 | 24.4 | 10.7 | 1.4 | 390/600/30 |
| 51 | K ₂ CO ₃ /ATM | 80 | 79 | 37.4 | 18.6 | 22.5 | 1.4 | " |
| 53 | ATM | 73 | 6 | 39.1 | 20.4 | 12.0 | 1.3 | " |
| 58 | Fe ₂ O ₃ /CS ₂ | 80 | 20 | 42.9 | 34.8 | 0.3 | 1.5 | " |
| 59 | AM/CS ₂ | 75 | 20 | 46.2 | 26.6 | 0.3 | 1.5 | " |
| 25 | None | 78 | 9 | | n.d. | | 1.3 | " |
| 26 | FeS | 81 | 7 | | n.d. | | 1.4 | " |
| 27 | NaAlO ₂ | 82 | 44 | | n.d. | | 1.4 | " |
| | | | | | | | | |
| 35 | K ₂ CO ₃ | 88 | 83 | 55.0 | 10.8 | 19.3 | 2.9 | 410/800/30 |
| 36 | K ₂ CO ₃ | 61 | 70 | 32.1 | 22.7 | 5.5 | 1.2 | 370/400/30 |
| 57 | NaAlO ₂ | 86 | 53 | 78.1 | 9.3 | -5.0 | 3.5 | 410/600/30 |

Figure 1 : Product Yield Distribution

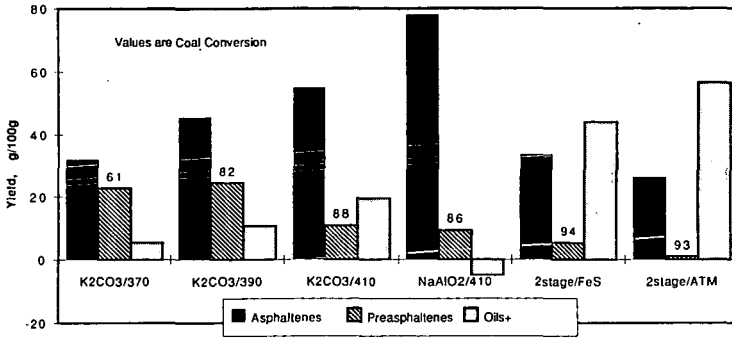


Figure 2 : Carbon Monoxide Utilization

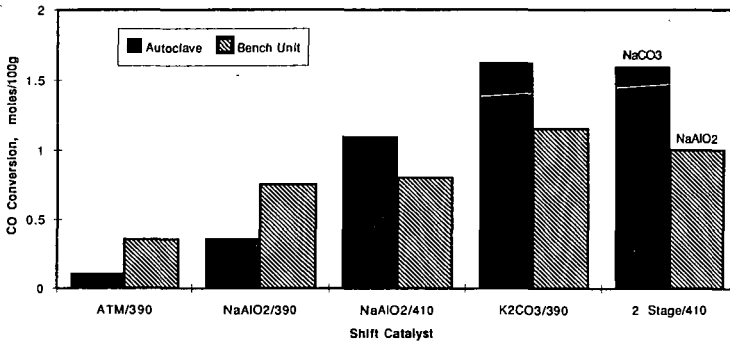
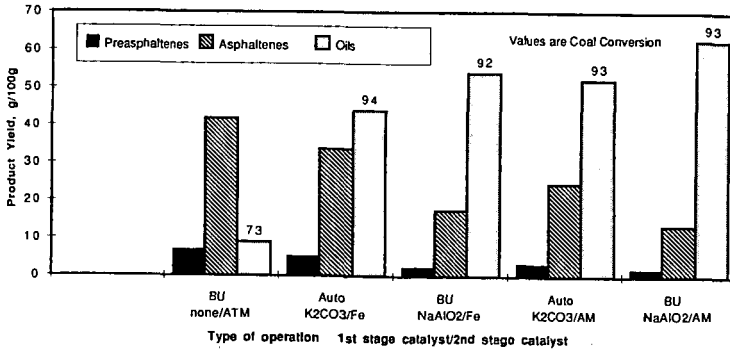


Figure 3 : Performance of Bench Unit vs. Autoclave (2 Stage)



TWO-STAGE LIQUEFACTION OF WYOMING SUB-BITUMINOUS COAL - EFFECT OF SYNGAS AS REDUCING GAS

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Keywords: Liquefaction, Sub-bituminous coal, Water-gas Shift Reaction

INTRODUCTION

The production of hydrogen constitutes one of the major operating cost components of a coal liquefaction process. Alternative sources of hydrogen such as synthesis gas, a mixture of CO/H_2 coming directly from a gasifier or steam reformer with minimum processing, can potentially improve the economic of a liquefaction plant. Also, it is known that in the presence of an alkali salt, $\text{CO}/\text{H}_2\text{O}$ is very effective in solubilizing high oxygen containing low rank coals at relatively mild severity conditions^{1,2}.

Non-alkali promoters, like iron⁴, cobalt/molybdate⁴⁻⁶ salts, were found to be active in enhancing the production of hydrogen through the water-gas shift (WGS) reaction. With the addition of H_2S , the presence of promoters had only a minor effect on coal conversion.⁵ In a two-stage direct coupled operations, in which activity of the second stage hydroprocessing catalyst can be severely reduced by alkali salts, it is necessary to explore non-alkali promoters for the WGS reaction. This paper discusses the work using a dispersed and a supported non-alkali promoter to catalyze the coal solubilizing step using a mixture of syngas and water.

PROCESS AND BENCH UNIT DESCRIPTIONS

Two-stage liquefaction tests were carried out in a bench scale continuous flow unit of nominal capacity of 1 Kg/h of coal feed. This unit was configured with two equal volume, fully backmixed reactors. Depending on the form of catalyst used, dispersed or supported, the first stage was operated either as a slurry reactor or an ebullated bed reactor. On the other hands, the second stage was utilized as an ebullated bed reactor. A simplified process flow diagram is shown in Figure 1. Coal dissolution occurred in the first stage in the presence of H_2 or CO/H_2 , while the primary liquids were further upgraded in the second catalytic stage under typical hydroprocessing conditions.

An interstage separator was used to remove excess syngas/water, light distillates and gaseous products generated from the coal solubilizing stage. Products from the second stage reactor were recovered as Separator and Atmospheric Still Overheads. Bottom materials from the Atmospheric Still, consisting of heavy distillates, unconverted coal and ash, was subjected to pressure filtration. The pressure liquid was recycled for slurring the coal feed. Sulfur additives can be injected to both stages.

CATALYST SCREENING

Several WGS promoters (sodium carbonate, sodium aluminate, iron oxides/DMDS, ammonium heptamolybdate(AHM)/DMDS, Amocat 1A/DMDS, Shell 317/DMDS) were evaluated using a 20 c.c. microautoclave at 399°C and 5.5 MPa cold CO pressure with and without solvent. CO and H_2O was charged at a molar ratio of 1/1. These catalysts were ranked according to the degree of the CO conversion. The relative activity ranking is:

Amocat 1A, Shell 317 > AHM > K_2CO_3 , NaAlO_2 >> Fe_2O_3

with or without solvent, as illustrated in Figure 2. Higher conversions were observed for tests with no solvent, it was probably due to better interaction between the reactants and the catalyst.

BENCH SCALE TESTS

Two bench runs were conducted to compare the activity of AHM and Shell 317 N/Mo extrudate catalyst as promoter for the coal solubilizing stage. In CMSL-03, AHM was premixed in the feed slurry at a concentration equivalent to 1500 wppm of Mo on a dry coal basis, while Shell 317 was loaded into the first reactor in CMSL-04. Due to the presence of the supported catalyst, the fluid volume in the first stage was 25% smaller in CMSL-04. Therefore, for the same feed rate a higher space velocity through the first reactor was anticipated in CMSL-04. The run conditions and performance of these two runs are compared in Table 1.

In the case of AHM, replacing H_2 with $CO/H_2/H_2O$ as reducing gas resulted in 2.5-3.0 W% higher coal conversion and a similar increase in distillate yield. Under similar operating conditions, in the presence of Shell 317, the improvement in performance by using syngas was less significant, less than 1.0 W%.

In comparing the performance of the first stage catalyst, AHM vs Shell 317, it is necessary to consider the different in fluid volume associated with each catalyst. The effective fluid volume was 25% lower in the case of the supported catalyst. As a result, at the same feed rate, both the coal conversion and distillate yield were lower when Shell 317 was used. Coal conversion reduced from 92.0 W% in CMSL-03 to 87.6 W% in CMSL-04, while the distillate yield declined from 64.6 to 58.5 W% under similar process conditions. However, as anticipated, Shell 317 was more effective in removing heteroatoms. Nitrogen removal was 10 W% more effective with Shell 317 than when AHM was used.

FIRST STAGE PRODUCTS

The first stage reactor samples exhibited a similar trend as the two stage products in term of conversion and product qualities, as shown in Table 2. The first stage coal conversion was higher in CMSL-03 than that of CMSL-04. Due to the hydrogenation function of the supported catalyst, both the solid and liquid products were richer in hydrogen and lower in heteroatoms.

Approximately, half of the distillates were generated from the first stage. The first stage distillates were heavier and contained higher boiling materials when syngas/water was used, as shown in Table 3. In CMSL-03 the H/C ratio declined from 1.65 and 1.59 when H_2 was replaced by CO/H_2 . It seems that the removal of nitrogen was more effective with CO/H_2 -AHM combination. The nitrogen content of the first stage distillate, 0.057 W%, was 3.8 times lower than when H_2 was used. However, such improved performance with CO/H_2 was not observed when supported catalyst was used as promoter.

ACKNOWLEDGEMENT

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Table 1 Performance on the Bench Tests

| <u>Process Conditions</u> | CMSL-03 1 | CMSL-03 2 | CMSL-04 1 | CMSL-04 2 |
|---|--------------|--------------|--------------|--------------|
| 1st Stage: | | | | |
| CO/H ₂ | 0/100 | 75/25 | 0/100 | 0/100 |
| Temperature, °C | 388 | 388 | 388 | 427 |
| Catalyst | AHM | AHM | Shell 317 | Shell 317 |
| 2nd Stage: | | | | |
| CO/H ₂ | 0/100 | 0/100 | 0/100 | 0/100 |
| Temperature, °C | 427 | 427 | 427 | 427 |
| Catalyst | Shell 317 | Shell 317 | Shell 317 | Shell 317 |
| <u>Process Performance, W% maf coal</u> | | | | |
| Coal Conversion | 89.5 | 92.0 | 86.8 | 87.6 |
| 514°C Conversion | 87.2 | 89.9 | 84.6 | 84.5 |
| C1-C3 | 6.50 | 6.56 | 6.30 | 7.65 |
| C4-524°C | 61.6 | 84.6 | 57.6 | 58.5 |
| H ₂ Used | 7.82 | 7.73 | 8.10 | 9.61 |
| HDN | 75.9 | 84.8 | 96.9 | 95.1 |

Table 2 Analysis of First Stage Reactor Samples

| <u>Process Conditions</u> | CMSL-03 1 | CMSL-03 2 | CMSL-04 1 | CMSL-04 2 |
|---------------------------|--------------|--------------|--------------|--------------|
| Coal Conversion, W% | 90.3 | 84.1 | 79.5 | 77.5 |
| H/C Ratio | | | | |
| Filter Liquid | 1.23 | 1.22 | 1.36 | 1.25 |
| Filter Solid | 0.57 | 0.65 | 0.94 | 0.89 |
| N in Filter Liquid | 0.57 | 0.50 | 0.22 | 0.35 |

Table 3 Analysis of First Stage Separator Overheads

| <u>Process Conditions</u> | CMSL-03 1 | CMSL-03 2 | CMSL-04 1 | CMSL-04 2 |
|----------------------------|--------------|--------------|--------------|--------------|
| API Gravity | 26.9 | 22.9 | 31.3 | 25.2 |
| IBP, °C | 85.0 | 83.3 | 88.3 | 95.0 |
| FBP, °C | 414 | 422 | 427 | 431 |
| ASTM D-86 Distillation, W% | | | | |
| IBP-177°C | 14.1 | 12.4 | 35.22 | 23.7 |
| 177-260°C | 10.3 | 10.5 | 9.43 | 10.5 |
| 260-343°C | 51.6 | 45.6 | 26.7 | 27.5 |
| 343°C | | | | |
| Elemental Analysis, W% | | | | |
| Carbon | 85.56 | 86.00 | 86.62 | 86.84 |
| Hydrogen | 11.74 | 11.37 | 12.67 | 11.67 |
| Sulfur | 0.079 | 0.086 | 0.015 | 0.043 |
| Nitrogen | 0.22 | 0.057 | 0.075 | 0.196 |
| H/C Ratio | 1.65 | 1.59 | 1.76 | 1.61 |

Figure 1 Schematic Process Flow Diagram of HRI's Two-Stage Liquefaction Bench Unit

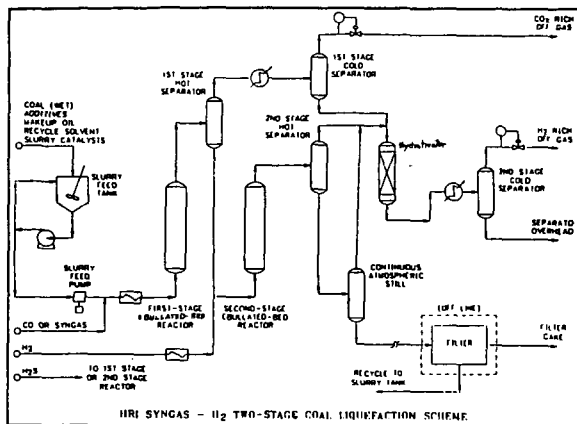
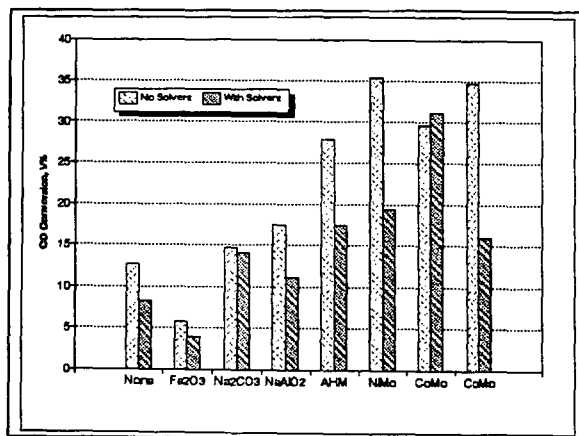


Figure 2 Activity of Promoter for the WGS Reaction



PREMIUM DISTILLATE PRODUCTS FROM DIRECT LIQUEFACTION OF COAL

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Key words: Coal, Liquefaction, Product Quality, Refining

INTRODUCTION

It has long been the prevalent impression that coal-derived liquids are heavy, viscous, aromatic, hetero-compound-rich, and very difficult and expensive to refine into transportation fuels. An extensive research and development program over the past two decades, sponsored by the U. S. DOE/PETC, has resulted in dramatic improvements in coal liquefaction product quality. High-quality coal-derived distillates are now obtainable from modern catalytic two-stage liquefaction (TSL) processes. Recently, the net products of four liquefaction runs that represent variations of state-of-the-art technology were characterized in detail. The four samples were generated at the Wilsonville 6 ton/day pilot plant (Runs 259G and 260D) and the Hydrocarbon Research Inc. (HRI) 2 lb/hr bench unit (Runs CC-15 and CMSL-2), as described in Table 1. Complete background and characterization data of the samples appear in the original reports of this work.¹⁻⁵

DISCUSSION

The distillation curves (Figure 1) of the four coal liquids have similar slopes over most of the boiling range, reflecting the similar fractional composition of the four liquids, despite the different feed coals and process conditions. All four liquids are resid-free and have end points (ca. 370-420 °C) much lower than those of early generation coal liquids. The HRI products are somewhat lower boiling than the Wilsonville products, partly as a result of different distillation operations. The specific gravities of these liquids range from 0.85 to 0.91, and the differences are primarily related to boiling range differences. These coal distillates possess excellent low-temperature characteristics: low viscosities (1.5-3.1 cSt @ 38 °C) and very low pour points (usually below -50 °C).

The four products are relatively high in hydrogen contents (11.2-12.7 wt %), and their H/C atomic ratios (1.54-1.74) are comparable to that of petroleum, resulting in fairly high characterization factors (10.9-11.1). The coal liquids have low N (0.03-0.3 wt %) and S (0.02-0.05 wt %) contents and contain negligible amounts of metals. The mid-percent curves of elements and hydrocarbon types in these coal liquids are plotted in Figures 2-8. For all four, the H content decreases gradually and the N content generally increases with increasing boiling point. The oxygen distribution shows a maximum in the 177-204 °C fraction, in which the single-ring phenols are concentrated. Sulfur content is very low throughout most of the boiling range. The N contents of the subbituminous coal liquids (W260D and CC-15) are higher than those of the bituminous coal liquids; this may reflect the use of only a single supported catalyst reaction stage in the subbituminous coal runs.

The aromatics content increases rapidly with increasing boiling point, yet these modern coal liquids are much less aromatic than early-generation liquefaction products. Figure 6 shows that it is feasible to produce from the coal liquids 30-40 LV% straight-run gasoline containing less than 22 LV% of aromatics, the projected specification for the turn of the century. These coal liquids contain approximately 60 LV% saturated hydrocarbons and the <177 °C naphthas contain as much as 91 LV% saturates. The paraffins level decreases substantially while naphthenes content decreases slightly with increasing boiling point. These liquids contain only about 3-5 LV% of olefins. Generally, the HRI liquids contain more H and less N, O, S, and aromatics over their boiling range.

The potential product yield structures of the four coal liquids are shown in Table 2. Clearly, only atmospheric distillation is required. The <177 °C naphtha yield is 24-28 LV%, with one exceptionally high case (CC-15) of 40 LV%. The yield of 204-288 °C light distillate, normally a diesel fuel fraction, is 34-36 LV%, except for W260D due to its high end point. The 177-204 °C swing cut (3.3-7.4 LV%) is also suitable for the recovery of single-ring phenolics. The yield of 288-343 °C heavy distillate, which can be refined into heavy diesel fuels/fuel oils or catalytically cracked/hydrocracked for gasoline and light diesel fuels, ranges from 18 to 26 LV%. The >343 °C atmospheric resid, which is equivalent to light vacuum gas oil and can be a part of the cracking feedstock, is less than 10 LV%, except for the high end-point W260D. These projections require verification by further refining studies of the coal liquids.

Major properties of the naphtha, light, and heavy distillates from these coal liquids are summarized in Tables 3-5 and compared with current ASTM and Federal

Phase I specifications and projected data for the year 2000. The aromatics and benzene contents of the naphthas are well below projected future specifications. This is a direct contradiction of the belief, no longer correct, that coal naphtha is highly aromatic. The olefins content (3-5 LV%) of the coal-derived naphthas is also very low compared with that of the current gasoline pool (about 10 LV%), and could readily meet projected future requirements. The octane numbers of the coal naphthas are within the range of straight-run naphthas from petroleum. The heteroatoms contents of the coal naphthas are low. They easily meet the current S specification and the HRI naphthas even meet the 1995 S requirement. The nitrogen levels are also low, particularly that of the CMSL-2 naphtha (0.01 wt %). Thus, the coal naphthas, after hydrofinishing, could be an excellent gasoline blending stock. Hydrotreating will simultaneously resolve the copper corrosion, oxidation stability, and existent gum deficiencies. The high-naphthene coal naphthas can also be good reformer feedstocks, if so required. In general, the coal naphthas exceed the 10% and 50% distillation-point maxima; however, this can always be adjusted through normal refinery blending operations.

The light distillates have excellent low-temperature properties (fr. pt. generally <-50 °C) and very low S contents, two advantages for jet fuel production. The major deficiency is high aromaticity, which must be reduced by high-severity hydrotreating. Compared to jet fuels, diesel fuel oils have much less stringent specifications and are thus easier to produce from coal distillates. In spite of the low cetane index, the very low S level makes the light distillates an attractive blending stock for the diesel pool. A moderate hydrotreatment may be needed to improve their stability and to benefit the cetane index. The heavy distillates qualify as a No. 4 diesel/fuel oil, meeting the low S requirement. They may also be considered as a feedstock for catalytic cracking or hydrocracking, and the >343 °C fraction can be included for this purpose. However, hydrotreating may be necessary to boost the H content for improved cracking behavior.

CONCLUSIONS

The net liquid products from modern coal liquefaction processes are lower boiling and have much lower end points (mostly under 400 °C) than crude petroleum. Coal liquids have very low concentrations of heteroatoms, particularly S, and metals, and are free of resids and asphaltenes. High yields of low-S (0.01-0.03 wt %) naphtha, kerosene, and diesel fuel fractions can be obtained simply by atmospheric distillation, with a total yield of light fuel fractions ranging from 68 to 82 LV% (W260D exclusive). The coal naphtha has a low aromatics content (5-13 LV%), readily meeting projected year-2000 requirements. Its low Reid vapor pressure allows light components from other sources to be blended. The coal light distillate of an appropriate boiling range will be a good low-S blending stock for the light diesel fuel pool. The heavy distillate can be refined into a low-S No. 4 diesel/fuel oil. This fraction, along with the >343 °C atmospheric bottoms, can be catalytically cracked or hydrocracked to make light liquid fuels. Thus, modern coal liquids should no longer be envisioned as thick liquids (or even solids) with high concentrations of aromatics and asphaltenes. Products obtained from advanced coal liquefaction technologies are more like light naphthene-base petroleum, but with lower heteroatoms and metals contents, and they are free of resids. Coal liquids are likely to be co-refined in existing petroleum refineries; and hydroprocessing of various severities would be needed for different fractions to produce quality blending stocks for refinery fuel pools.

CURRENT DEVELOPMENTS

DOE continues to support work on improving and evaluating product quality. Additional detailed product inspections are planned. A newly initiated program will include actual refining and testing of the refined products. A recent development in coal liquefaction technology is to include in-line fixed-bed hydrotreating of the products. The resultant liquid products are expected to be of even higher quality for conversion into transportation fuels.

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Table 1. Sources of Coal Liquid Samples

| Plant/Run | Feed Coal | Process Description |
|------------------|------------------------|--|
| Wilsonville 259G | Pittsburgh Seam | Catalytic/Catalytic Shell 324 441/421 °C |
| Wilsonville 260D | Wyodak and Anderson | Catalytic/Thermal Shell 324 421/412 °C |
| HRI CC-15 | Wyodak and Anderson | Thermal/Catalytic Shell 317 427/413 °C |
| HRI CMSL-2 | Illinois No. 6 | Catalytic/Catalytic Shell 317 400-414/424-433 °C |

Table 2. Potential Product Yield Structures

| Boiling Range, °C | Coal Liquids Yield, LV % | | | |
|-------------------|--------------------------|-------|-------|--------|
| | W259G | W260D | CC-15 | CMSL-2 |
| IBP-177 | 26.7 | 24.4 | 40.2 | 27.9 |
| 177-204 | 6.4 | 3.3 | 7.4 | 5.7 |
| 204-288 | 35.5 | 22.6 | 34.9 | 34.4 |
| 288-343 | 21.7 | 17.9 | 17.5 | 25.6 |
| >343 | 9.7 | 31.8 | -- | 6.3 |

Table 3. Characteristics of Coal-Derived Naphtha Fractions

| Properties | W259G 18P-193°C | W260D 18P-193°C | CC-15 18P-193°C | CMSL-2 18P-177°C | Current ¹ Gasoline Specifications | Federal Phase I (1995) | Projected (2000) |
|--|--------------------|--------------------|--------------------|---------------------|--|------------------------------|---------------------|
| Specific Gravity @ 15.6°C | 0.7844 | 0.7758 | 0.7798 | 0.7771 | | | |
| Elemental Analysis, wt% | | | | | | | |
| H | 13.3 | 13.6 | 14.0 | 14.2 | 0.1 max | 0.03 max | 0.003 max |
| S | 0.05 | 0.08 | 0.03 | 0.01 | | | |
| N | <0.1 | 0.1 | 0.09 | 0.01 | | | |
| Basic N | 0.028 | 0.046 | 0.082 | 0.006 | | | |
| Hydrocarbon Group, LV% | | | | | | | |
| Paraffins | 19.3 | 188.0 | 38.0 | 36.9 | 25 max | 22 max | 4.0 max |
| Naphthenes | 67.5 | | 45.7 | 53.9 | | | |
| Aromatics | 13.2 | 7.0 | 8.7 | 5.3 | | | |
| Olefins | -- | 5.0 | 4.6 | 3.2 | | | |
| Benzene | -- | -- | 0.089 | 0.20 | | | |
| Octane, Research | -- | -- | 61.6 | 60.1 | | | |
| Octane, Motor | -- | -- | 60.7 | 58.7 | | | |
| Octane, by GC | 86.5 | 87.1 | 74.8 | 75.2 | | | |
| Reid Vapor Pressure, psi | 2.8 | 3.1 | 2.54 | 2.74 | 9.0 max | 9 max ² | |
| Copper Corrosion | 1a | 1a | 3b | 3b | 1 max | | |
| Existent Gum (Washed), mg/100 ml | 7.6 | 40.2 | 11.2 | 1.0 | 5 max | | |
| Oxidation Stability (0525), minutes | pass | fail | 105 | 1440 | 240 min | | |
| DBP Distillation, °C | | | | | | | |
| 10% | 91 | 80 | 88 | 96 | 70 max | | |
| 50% | 126 | 115 | 123 | 127 | 77-121 | | |
| 90% | 172 | 171 | 169 | 166 | 190 max | | 149 max |

¹Class A²Northeastern States

Table 4. Characteristics of Coal-Derived Light Distillates

| Properties | W259G 193-266°C | W260D 193-266°C | CC-15 193-266°C | CMSL-2 177-204°C 204-288°C | | Jet A Specs | No. 2 Diesel Fuel Specs |
|-------------------------------|--------------------|--------------------|--------------------|----------------------------------|--------|----------------------|----------------------------|
| Specific Gravity @ 15.6°C | 0.8990 | 0.9260 | 0.8899 | 0.8492 | 0.8890 | 0.775-0.840 | |
| Elemental Analysis, wt% | | | | | | | |
| H | 11.5 | 10.6 | 11.77 | 12.72 | 12.27 | 0.3 max ¹ | 0.50 max ¹ |
| S | 0.04 | 0.04 | 0.03 | 0.01 | 0.01 | | |
| N | <0.1 | 0.3 | 0.33 | 0.03 | 0.03 | | |
| Basic N | 0.093 | 0.22 | 0.27 | 0.023 | 0.029 | 0.003 max | |
| Mercaptan S | 0.003 | 0.009 | 0.0045 | 0.0019 | | | |
| Hydrocarbon Group, LV% | | | | | | | |
| Paraffins | -- | 147.0 | 9.6 | 7.5 | 7.5 | 25 max | |
| Naphthenes | -- | | 43.1 | 61.3 | 53.0 | | |
| Aromatics | 44.0 | 50.0 | 41.4 | 28.4 | 37.5 | | |
| Olefins | 3.0 | 3.0 | 5.8 | 2.8 | 2.0 | 3 max ² | |
| Naphthalene | -- | 4.94 | 4.23 | 0.48 | -- | | |
| Viscosity, cSt @ 38°C | -- | -- | -- | -- | 2.50 | 8.0 max | 1.9-4.1 |
| -20°C | 1.75 | 18.94 | 10.80 | 4.68 | -- | | |
| Freezing Pt., °C | -53.5 | too dark | -24.4 | -72.8 | -- | -40 max | |
| Smoke Pt., mm | 10.8 | 9.8 | 10.9 | 15.6 | -- | 25 min ² | |
| R Reid Vapor Pressure, psi | 0.2 | 0.0 | <0.01 | 0.02 | -- | | |
| Thermal Stability (JFTOT) | Fail | -- | Fail | -- | -- | | |
| Copper Corrosion | 1a | 1a | 1a | 1a | 1a | 1 max | 3 max |
| Net Heat of Combustion, MJ/kg | 42.1 | 42.0 | 41.7 | 42.8 | -- | 42.8 min | |
| Cetane Index | 22.9 | 21.8 | 26.4 | 20.8 | 32.7 | | 40 |

¹Reduced to 0.1 wt% in Federal Phase I.²For smoke point 70 mm (min) and naphthalene 3 LV% (max).³Reduced to 0.05 wt% in Federal Phase I.

Table 5. Characteristics of Coal-Derived Heavy Distillates

| Properties | W259G 266°C ^a | W260D 266-343°C | CC-15 266-337°C | CMSL-2 288°C ^a | No. 4-D Diesel Fuel Specs | No. 4 Fuel Oil Specs |
|---------------------------|-----------------------------|--------------------|--------------------|------------------------------|------------------------------|-------------------------|
| Specific Gravity @ 15.6°C | 0.9574 | 0.9484 | 0.9223 | 0.9262 | 0.8762 min | |
| Elemental Analysis, wt% | | | | | | |
| H | 10.5 | 10.7 | 11.4 | 11.8 | 2.00 ¹ | |
| S | 0.04 | 0.03 | 0.01 | 0.01 | | |
| N | 0.2 | 0.3 | 0.22 | 0.06 | | |
| Basic N | 0.093 | 0.22 | 0.19 | 0.03 | | |
| Hydrocarbon Group, LV% | | | | | | |
| Paraffins | | | 10.1 | | | |
| Naphthenes | | | 34.5 | | | |
| Aromatics | | | 52.1 | | | |
| Olefins | | | 3.3 | | | |
| Viscosity, cSt @ 38°C | 8.97 | 6.2 | 5.34 | 8.77 | 5.5-24.0 ² | 5.5-24.0 ² |
| Pour Pt., °C | | | 1.7 | -12 | | -6 max |
| Copper Corrosion | 1a | 1a | 1a | 1a | | |
| Flash Pt., °C | | 124 | 136 | | 55 min | 55 min |
| Cetane Index | 26.5 | 27.7 | 34.2 | 35.2 | 30 | |

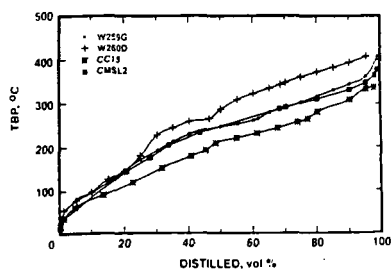
¹Low sulfur specification 0.05 wt% at 40°C

Figure 1. True-Boiling-Point Curves of Two-Stage Coal Liquids

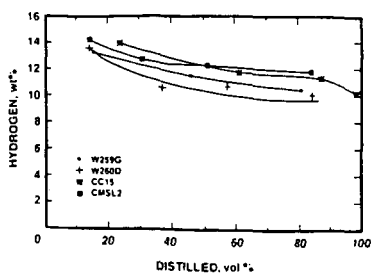


Figure 2. Hydrogen Mid-Percent Curves of Coal Liquids

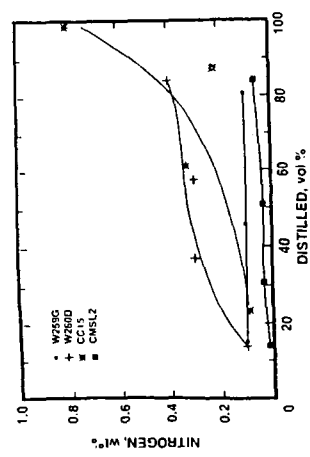


Figure 3. Nitrogen Mid-Percent Curves of Coal Liquids

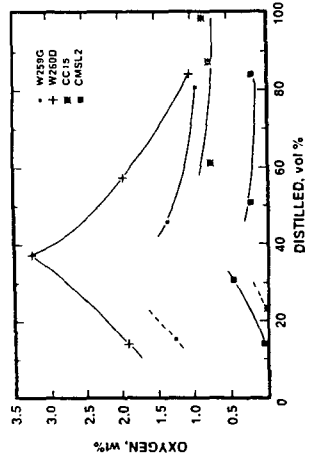


Figure 4. Oxygen Mid-Percent Curves of Coal Liquids

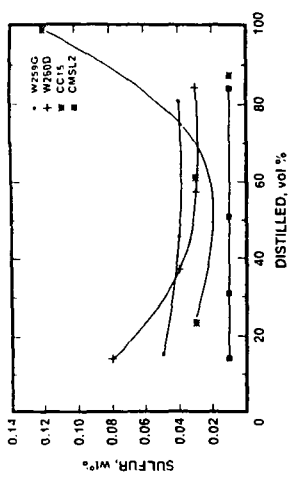


Figure 5. Sulfur Mid-Percent Curves of Coal Liquids

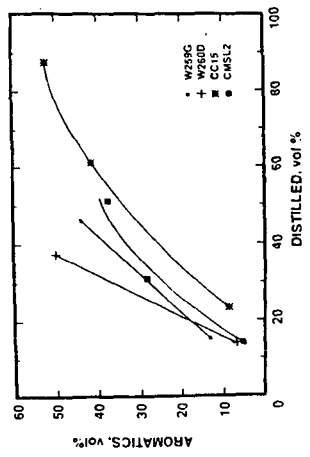


Figure 6. Aromatics Mid-Percent Curves of Coal Liquids

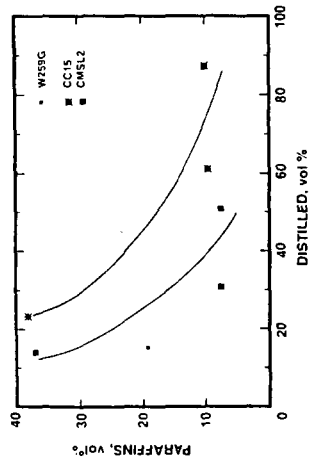


Figure 7. Paraffins Mid-Percent Curves of Coal Liquids

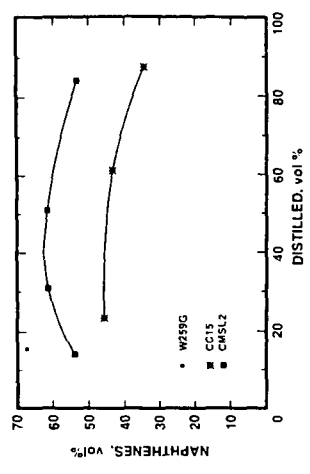


Figure 8. Naphthenes Mid-Percent Curves of Coal Liquids

Valuation of Coal Liquids as Refinery Feedstocks Using Linear Programming Tool (PIMS)

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ABSTRACT

Product pricing follows the simple law of supply and demand, and therefore, it is extremely dependent on the market situation. As long as the identifiable market is established, product valuation should not be complicated. Because of the inherent characteristics of coal liquefaction products, however, direct marketing of coal liquid products to the end user may not be feasible. For coal liquid products, the market is primarily through the refinery. The purpose of this paper is to demonstrate the proper method of evaluating the economics of coal liquids as refinery feedstocks.

The approach of having a dedicated refinery to upgrade coal liquids to marketable products may not be a practical solution. When the products are brought into an existing refinery with a certain configuration already built in, the obvious question will then be how best the product can be routed to the various processing sections of the refinery to obtain the maximum margin for the various coal liquids. In addition, the coal liquid products are envisioned to be routed to more than one refinery in order to maximize product value. This complex scheme could be optimized by the application of linear programming (LP) method. However, because of the complexity of the situation, the success of the product pricing evaluation is very much dependent on the type of LP tool being used. In this paper, the LP tool utilized is Bechtel's proprietary linear programming tool, called Process Industry Modeling Systems (PIMS). The approach described in the paper utilizes PIMS in assigning value to various products obtained by direct liquefaction of coal.

INTRODUCTION

Depending on the complexity of the problem, there are three (3) possible ways of assessing product valuation and economic analysis in a refining environment. These three possible ways are: Back of the envelope calculations, application of Lotus (or similar) worksheets and utilization of LP-based optimization.

Back of the envelope type calculations could be sufficient for a topping refinery. Likewise, a Lotus worksheet tool may be suitable for a hydroskimming refinery. As combinations of crudes are processed in a refinery, and as the refinery configuration becomes more complex, it becomes difficult, if not impossible, to conduct a reasonably decent analysis by following either of the above mentioned two methods. In such situations, linear programming (LP) becomes, the only practical option of choice for such calculations.

The objective of this paper is to show how an LP system (PIMS) can be used effectively in determining the relative value of the coal liquids as they relate to a petroleum refinery as a feed stock. In a given refinery PIMS is able to assess the global effects of processing and/or blending the various coal liquids, either as a total mixture or as separate fractions.

PRODUCT VALUATION BY LINEAR PROGRAMMING (PIMS)

Typically the linear programming tool, PIMS, takes into account an array of data such as: product prices, crude oil price, utility costs, crude oil assays and characterization data (API, sulfur, distillation, octane number, Cetane number, Bromine number, etc.).

When coal liquid is brought in as feed to a given refinery, PIMS allows the optimum disposition of the feed and assign the value of the coal liquid products with reference to the petroleum feed. The product valuation scheme is schematically shown in Figure 1.

Bases and Assumptions

Methodology - The evaluations have been conducted using Bechtel's proprietary LP system, PIMS (Process Industry Modeling Systems). The approach to the economic analysis is based on the break-even value concept, i.e., that value of incremental volume of coal liquid that will result in no monetary loss (or gain) compared to the current, i.e., base case. The

resulting product value is then expressed in terms of its syncrude premium ratio (SCP) relative to the price of PAD-II crude mix.

Refinery Configuration - The refinery LP model emulates a typical PAD-II district configuration (Refer to Fig. 2). Rated capacities of various process units are indicated in Table 1.

Prices/Volumes - The prices of feedstocks and finished products, including appropriate limits on supply and demand, were based on the recent DOE Study on direct liquefaction of coal (DOE Contract No. DEAC22 90PC89857) conducted by Bechtel.

Unit Capacities - The refinery is rated at 150 MBPD total crude charge (130 MBPD PAD-II, 20 MBPD Alaskan North Slope).

Case Definitions

The volume of the coal liquid mixture is estimated to be 30,973 BPSD, and consists of the following:

| | | | <u>LV%</u> |
|-----|-----------|---------------------|------------|
| MNC | C5-350°F | Coal Naphtha | 31.0 |
| LDC | 350-450°F | Coal Lt Distillate | 12.6 |
| HDC | 450-650°F | Coal Hv Distillate | 34.9 |
| LVC | 650-850°F | Coal Lt Vac Gas Oil | 21.5 |
| | | Coal Liquid Mix | 100.0 |

The cases are separated into two broad categories. These two categories designated as A and B are defined below:

- A Production is limited by market demand, and
- B All products can be sold in the marketplace.

The individual cases are then further defined as follows:

- Case 1 Base Case, Zero Coal Liquids
- Case 2 100% Coal Liquid Mix
- Case 3 100% Coal Naphtha
- Case 4 100% Coal Lt Distillate
- Case 5 100% Coal Hv Distillate
- Case 6 100% Coal Lt Vac Gas Oil

Processing Coal Liquids in a PAD-II Refinery

Coal naphtha (MNC) is fed to the Reformer and converted into high-octane reformat. Light distillate (LDC) is blended into finished diesel and finished fuel oil. Heavy distillate (HDC) is sent to the Cat Cracker as well as directly to diesel and fuel oil blending. Light vacuum gas oil (LVC) is used as a fuel oil blending component and as a Cat Cracker feedstock.

Results and Discussions

The product valuation for coal liquid was conducted utilizing the PIMS model described above. A typical PADD II refinery configuration and crude mix with a fixed price were used and assuming that the various fractions of coal liquid are available to the refinery. It was also assumed that the naphtha fraction of the coal liquid (C5-350°F) was sent to the reforming unit, the light distillate fraction (350-450°F) was sent for blending (diesel and fuel oil), the heavy distillate fraction (450-650°F) was available for diesel and fuel oil blending and also used as FCCU feed, and the vacuum gas oil (650-850°F) was used as fuel oil blending stock and FCCU feed. The product valuation was then calculated under two distinct scenarios. These two scenarios are: 1) force the refinery to make the same product slate that would make on its typical crude oil feed and 2) allow the product slate to float to maximize the profit. The product valuation, was expressed as the syncrude premium factor (SCP) which relates the coal liquefaction plant product values to a typical crude oil in PAD II refinery.

A low SCP value of 1.07 was determined for scenario 1 and 1.27 for scenario 2 described above. In actual case SCP can range anywhere between these two limits.

The SCP is ultimately used to calculate the economics of coal liquefaction where the economics is expressed in terms of crude oil equivalent price. Figure 3 depicts a interrelationship of various models developed in the previously referred DOE study on direct liquefaction of coal. The crude oil equivalent price is observed to be very sensitive to the value of SCP. When SCP was changed from 1.07 to 1.27 in the earlier referred DOE study on direct liquefaction of coal it was observed that the crude oil equivalent price reduced by \$5.35. The result indicates that the accurate determination of SCP is important. The refinery model itself and the input data utilized in PIMS need to be carefully examined to make a better assessment of SCP. Recently a refining end use study has been funded by DOE whereby Bechtel Corporation (contractor) in conjunction with a number of subcontractors has started updating the PIMS preliminary baseline model and the coal liquid products characterization data.

Table 1
Rated Capacities of Various Process Units

| Refinery Unit | Rated Capacity* |
|----------------------|-----------------|
| Crude Unit #1 | 130,000 |
| Crude Unit #2 | 20,000 |
| Vacuum Unit #1 | 59,300 |
| C5/C6 Isomerization | 11,200 |
| Naph Hydrotreater | 45,900 |
| Low-P Reformer | 39,400 |
| Kero Hydrotreater | 6,000 |
| Dist Hydrotreater | 15,300 |
| Catalytic Cracker | 53,300 |
| Sulf Acid Alkylation | 11,900 |
| Hydrocracking (Dist) | 7,500 |
| H2 Plant MMSCFD | 0.030 |
| Delayed Coker | 16,800 |
| Sulfur Plant MLT/D | 0.070 |

*All rated capacities unless listed, are in BPD

Figure 1
PIMS Product Valuation Scheme

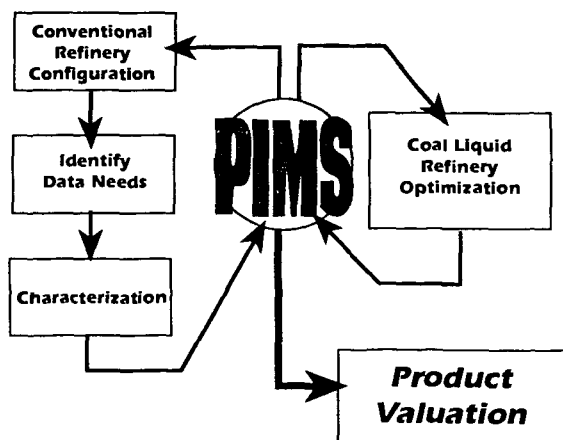


Figure 2
Coal Liquefaction Product Disposition
Scheme for a Given Refinery

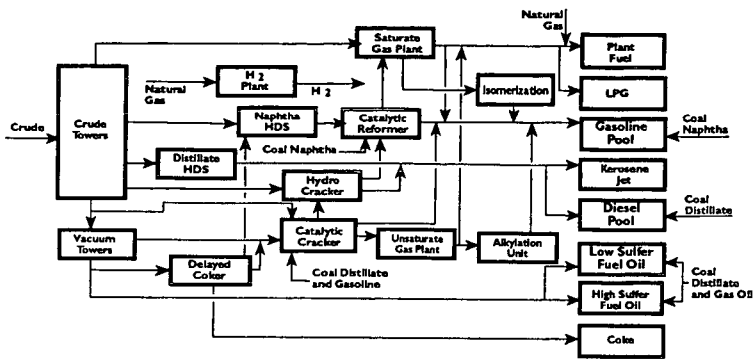
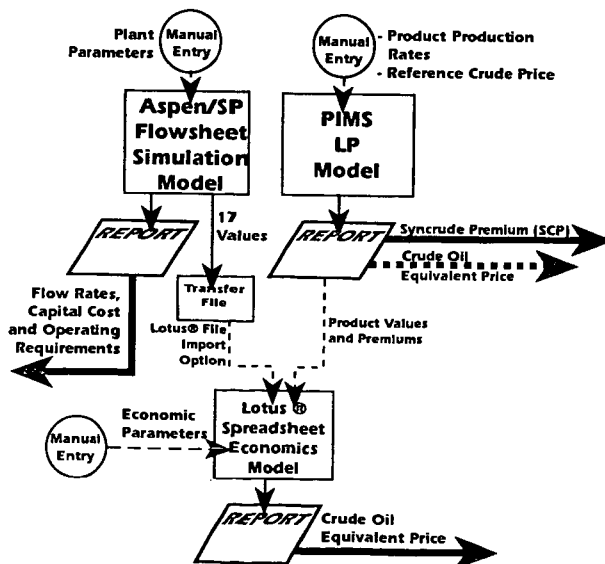


Figure 3
Interrelationship of Various Models
Developed in DOE Study on Direct Liquefaction of Coal



TECHNOECONOMIC ASSESSMENT OF DEWAXING & HYDROTREATING RECYCLE DISTILLATE SOLVENT IN SUB-BITUMINOUS COAL LIQUEFACTION

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Keywords: Coal Liquefaction, Solvent Quality, Economics

INTRODUCTION

During Wilsonville pilot plant Runs #262 and #263 with Black Thunder sub-bituminous coal, waxy deposits were found in the distillate streams of the Two Stage Liquefaction process unit(1). The quality of the distillate portion of the recycle solvent stream from these two runs was poor(2). This result indicated the potential for improving overall liquefaction performance and economics by treating the waxy distillate recycle solvent stream. This is one of the areas of liquefaction being studied under a DOE sponsored contract by a group headed by the Center for Applied Energy Research of the University of Kentucky. CONSOL Inc., Sandia National Laboratories and LDP Associates are the other organizations participating in this project. The technical approach taken to improve the solvent quality of this distillate is to first, dewax it using the commercially proven solvent dewaxing technique, followed by conventional hydrotreatment to improve the materials donor capabilities.

DESCRIPTION OF SYSTEM

A simplified block flow diagram of the dewaxing and hydrotreating processes is shown in Figure 1. Coal and a three-stream-recycle process solvent are fed to the liquefaction unit. The heaviest product from the liquefaction reaction system is fed to a vacuum tower which separates a heavy distillate fraction from the ash-containing residue fraction. Part of the ashy residue is recycled while a smaller portion is fed to a ROSE unit where the net ash fed to the system is removed and a clean resid material is recovered and recycled. The 650°F+ heavy distillate stream from the vacuum tower is at least partially dewaxed and hydrotreated before being recycled back to the liquefaction system. In Wilsonville operation the analogous heavy distillate stream was recycled to liquefaction without either dewaxing or hydrotreating.

DEWAXING

Testing at CONSOL indicated that the solvent quality of the heavy distillate stream was significantly improved after solvent dewaxing(2). In the dewaxing step a solvent is used to precipitate and filter out the wax species at below atmospheric temperature. Solvent Dewaxing (SDW) is a commonly applied technique in the petroleum refining industry to remove paraffinic hydrocarbons from lube oil stocks(3). The waxy material or slack wax removed in the Dewaxing unit is highly paraffinic (Figure 2). When additional processing steps (deoiling & hydrotreatment) are used a high value, fully refined paraffin wax can be produced from the slack wax(4). Alternatively, the

highly paraffinic slack wax stream can be sent to a fluid cat cracking (FCC) unit where it is readily converted into gasoline and other refinery type byproducts.

DEWAXED OIL HYDROTREATING

Experimental work done at Sandia indicated that further improvement in solvent quality could be obtained by fixed bed hydrotreating the dewaxed oils(5). The objective of the hydrotreatment is to add about 1% hydrogen to the dewaxed distillate solvent which will subsequently be donated to the coal in the first stage liquefaction reactor. Since hydrogenation of aromatics occurs rapidly, mild operating conditions are anticipated (e.g. LHSV = 1, 1,800 psi & 750°F max.).

Data from a projected commercial scale EDS solvent hydrotreater was utilized to evaluate the cost of dewaxed oil hydrotreating(6). Estimated annualized hydrotreating costs are shown in Table 2. A 50% increase in space velocity only reduces liquefaction unit gasoline product cost by a relatively insignificant 9¢/Bbl.

TECHNOECONOMIC ASSESSMENT

A cost-benefit analysis is being used to determine an economical level of wax in the distillate recycle solvent for projected commercial operation. A good indicator of solvent quality is the concentration of alkyl beta (paraffinic) protons (ABP) in the stream. As shown in Table 1, the recycle distillate solvent stream (V-1074) in Wilsonville Run #263J contained 32.9% ABP's. Using the CONSOL experimental batch SDW data and commercial SDW information, estimated steady-state simulations of commercial SDW operations were developed as a function of the amount of the distillate solvent fed to the dewaxer. As the proportion of distillate fed to the dewaxer increases, the ABP concentration of the dewaxed oil decreases (Figure 3) and its quality as a solvent increases. Unfortunately, SDW costs also increase with increasing feedrates. Because of the rapid drop in ABP concentration versus SDWU feedrate, two SDWU feedrate cases (25% & 100%) were evaluated.

Summary data for the two Solvent Dewaxing Unit (SDWU) feed cases is shown in Table 3. Two slack wax byproduct disposition scenarios were also evaluated at each SDWU feedrate. The first scenario assumes that all of the slack wax byproduct can be sold as fully refined paraffin wax (FRPW) after the appropriate processing steps. In the second scenario it is assumed that the sale of FRPW is limited to 10% of the U.S. wax market demand. In this case, some as-is slack wax is sold to the construction industry (10% of market demand), with most of the slack wax sold as lower value FCC feedstock. The values of the FRPW, slack wax for the construction industry and slack wax as FCC feedstock are all related to crude oil price and are shown in Table 3. FCC feedstock price was determined from the expected yield structure with slack wax feed (62 vol.% gasoline), estimated product prices (e.g. gasoline @ \$40/Bbl) less estimated FCC processing costs (\$2/Bbl). The almost three times higher value of the specialty FRPW versus the commodity type FCC feedstock value results in huge differences in SDWU revenue between

the All-Wax and 10% Wax cases. When 100% of byproduct sales are as FRPW, the cost of SDW is exactly offset by the value of the FRPW sales for the 100% feed case. An even more favorable result occurs for the 25% feed case. FRPW sales exceed SDWU costs thereby reducing liquefaction plant gasoline product cost by 52¢/Bbl. even before taking into account the benefits of using the improved distillate solvent in liquefaction. Thus if the All-Wax byproduct disposition scenario is valid, the use of a SDWU is highly desirable.

However, in a five sub-bituminous coal liquefaction plant scenario, the amount of FRPW produced would be a significant portion of the total U.S. wax market demand. At a low wax market penetration of 10%, SDWU costs exceed byproduct revenues by \$1.16/Bbl of gasoline for the 25% feed case and by \$3.27/Bbl for the 100% feed case.

The above results range from a decrease in liquefaction plant gasoline product cost of 52¢/Bbl for the 25% feed-100% wax sales case to an increase of \$3.27/Bbl for the 100% feed-10% wax market penetration case. These results indicate the extremely significant effect byproduct disposition and SDWU feedrate have on SDWU economics.

Hydrotreating the dewaxed oil is estimated to increase overall costs by approximately \$1.16/Bbl of liquefaction plant gasoline product in all cases.

Therefore, the estimated total net cost for SDW and Hydrotreating the distillate portion of the recycle solvent ranges from a low of 65¢/Bbl for the All-Wax, 25% feed case to a high of \$4.42/Bbl for the 10% Wax, 100% feed case.

FUTURE WORK

The benefit to the liquefaction system of using the better dewaxed and hydrotreated distillate solvent is being evaluated. It seems likely that the benefit of using dewaxing and hydrotreating will lie in between the respective costs of the All-Wax and 10% Wax cases at each SDWU feedrate. In addition, the use of Catalytic Dewaxing (CDW) instead of SDW will be evaluated. In CDW the waxy substances are directly cracked to lighter boiling range distillates and no waxy byproduct is produced.

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TABLE 1
DISTILLATE SOLVENT (V-1074) PROPERTIES
WILSONVILLE RUN # 263J
BLACK THUNDER COAL, HYBRID MODE OPERATION

| | |
|--------------------------------------|---------------|
| WEIGHT RATIO TO MF COAL : | 0.858 |
| ESTIMATED SPECIFIC GRAVITY : | 1.04 (4.6API) |
| ESTIMATED ELEMENTAL ANALYSIS , Wt. % | |
| - Carbon | 89.28 |
| - Hydrogen | 9.49 |
| - Oxygen | 0.76 |
| - Nitrogen | 0.44 |
| - Sulfur | 0.03 |
| BOILING RANGE, OF : | 650 to 1,000 |
| ESTIMATED WATSON "K" FACTOR : | 10.5 |
| PROTON NMR DISTRIB'N (CONSOL), %: | |
| - Condensed Aromatics | 13.9 |
| - Uncondensed Aromatics | 4.4 |
| - Cyclic Alpha | 14.3 |
| - Alkyl Alpha | 8.2 |
| - Cyclic Beta | 14.5 |
| - Alkyl Beta | 32.9 |
| - Gamma | 11.8 |
| SOLVENT QUALITY(CONSOL) : | 70.9 |

(1.5/1 SOLVENT-TO-COAL, INDIANA V COAL, 750 F, 30 MINUTES)

TABLE 2
ECONOMICS OF DEWAXED OIL HYDROTREATING
ESTIMATED ANNUAL HYDROTREATER COST

BASIS:

- 83,900 BPSD Feedrate
- Wyoming Plant Location
- Mid - '92 Dollars per Barrel of Gasoline Product
- 15% Estimating Allowance on Capital Costs
- 0.15 Capital Charge Factor
- 320 Operating Days per Year
- Two Year Catalyst Life
- Costs of Makeup Hydrogen & Purge Hydrogen Excluded

| | 1.0 | 1.5 |
|---------------------------------|-------------|-------|
| Annualized Capital Cost : | 0.874 | 0.805 |
| Catalyst Replacement @ \$3/lb : | 0.068 | 0.045 |
| Electrical Power @ 4¢/kw-hr : | 0.085 | 0.085 |
| Fuel Gas @ \$2/MMBtu : | 0.104 | 0.104 |
| Operating Labor : | 0.023 | 0.023 |
| Total = | 1.154 | 1.062 |
| LHSV Δ = | \$0.092/Bbl | |

TABLE 3
BLACK THUNDER LIQUEFACTION STUDY
DEWAXING & HYDROTREATING
THE DISTILLATE PORTION OF PROCESS SOLVENT
ECONOMIC EVALUATION OF NET COSTS

• BASIS

- Liquefaction : Five Plants @ 50,000 BPSD of Gasoline Each
- Wax Yield : 4% of MAF Coal
- Wax Cracking Rate : 22% of Wax Circulating
- Crude Oil Price : \$ 30/ Bbl.
- Gasoline Price : \$ 40 / Bbl.
- Wax Value : 34.3 ¢ / lb.
- Slack Wax Value : 18.8 ¢ / lb.
- FCC Feed Value : 11.5 ¢ / lb.

• TOTAL PRODUCTION DATA

| | All Wax | | Wax = 10% of Market | |
|----------------------------|---------|---------|---------------------|---------|
| - Product Distribution | | | | |
| - % of Feed to DWU | 25% | 100% | 25% | 100% |
| - Fully Refined Wax, T/Yr. | 462,000 | 737,500 | 60,700 | 60,700 |
| - Slack Wax, T/Yr. | None | None | 67,200 | 67,200 |
| - FCC Feed, T/Yr. | None | None | 415,600 | 729,000 |

• ECONOMIC DATA PER PLANT

| | | | | |
|---------------------------------------|--------|--------|--------|--------|
| - Esfd DWU Capital Cost, \$ MM | 236 | 463 | 180 | 410 |
| - Capital Savings in Upgrading | - 24 | - 39 | - 30 | - 64 |
| - Net Capital Cost, \$ MM | 212 | 424 | 150 | 346 |
| - DWU Product Revenue, \$ MM/Yr. | 63.4 | 101.2 | 32.5 | 46.9 |
| - Decreased Gasoline Revenue | - 23.6 | - 37.6 | - 27.8 | - 43.8 |
| - Increase in Revenue, \$ MM/Yr. | 39.8 | 63.6 | 4.7 | 3.1 |
| - Net Annual'd Δ in Cap. Cost* | 31.8 | 63.6 | 22.5 | 51.9 |
| - Net Dewaxing Cost, \$ MM/Yr. | - 8.0 | None | + 17.8 | + 48.8 |
| - Net Dewaxing Cost, \$ / Bbl. | - 0.52 | None | + 1.16 | + 3.27 |
| - Hydrotreater Cost, \$ / Bbl. | + 1.17 | + 1.15 | + 1.17 | + 1.15 |
| - Net Δ in Gasoline Cost, \$ / Bbl.** | + 0.65 | + 1.15 | + 2.33 | + 4.42 |

* ASSUMING 15% CAPITAL CHARGE FACTOR

** NOT INCLUDING BENEFITS OF USING THE IMPROVED SOLVENT IN THE LIQUEFACTION UNIT

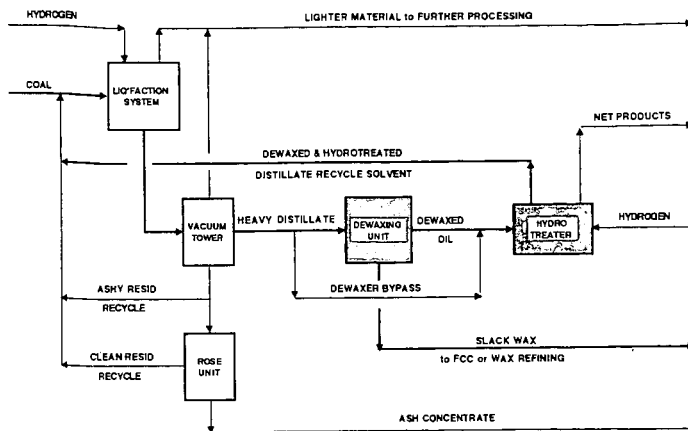


FIGURE 1
SIMPLIFIED BLOCK FLOW DIAGRAM
DEWAXING & HYDROTREATING OF DISTILLATE RECYCLE SOLVENT

TEXACO DEVELOPMENT CORPORATION TWO STAGE SOLVENT DEWAXING UNIT WITH INCREMENTAL DILUTION

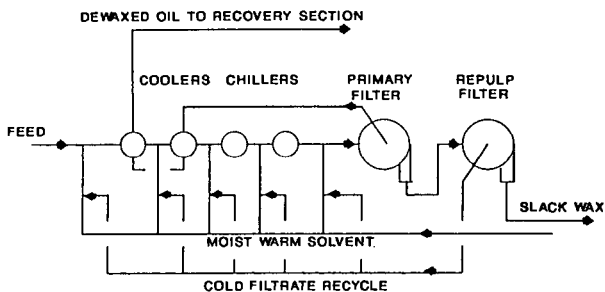
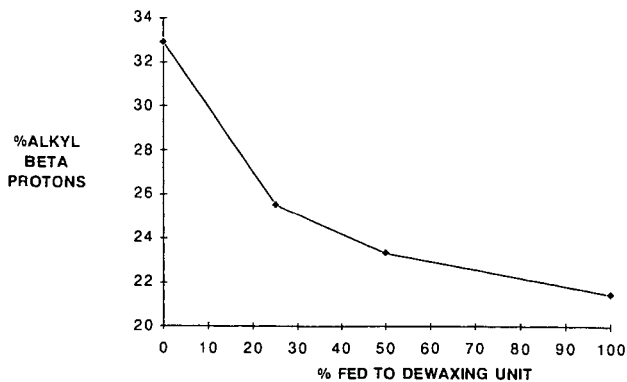


FIGURE 2

FIGURE 3 EFFECT OF DEWAXING UNIT BYPASS



ALTERNATE ROUTES FOR THE PRODUCTION OF FUELS FROM COAL AND NATURAL GAS

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Keywords: Coal Liquefaction, Gasification, Fischer-Tropsch Synthesis

ABSTRACT:

Almost all transportation worldwide is powered by high energy density liquid hydrocarbon fuels produced from crude oil. Transportation fuels currently use over 50 percent of total world petroleum demand of 66 million barrels per day. Prior MITRE studies indicate that crude oil supply will become severely limited after the year 2030 as increasing world energy demand, driven by population growth and economic development, depletes oil resources. If conventional liquid hydrocarbon fuels that can use existing production and distribution infrastructures are still needed for transportation in the future, then alternate sources of these fuels will have to be utilized. Two such sources are natural gas and coal. Natural gas reserves worldwide are expected to last well into the 21st century, and coal resources are enormous. This paper examines the technologies for producing environmentally superior liquid transportation fuels from coal and natural gas using modern conversion technologies. Estimates of the costs of fuels from these sources are given, and the potential environmental impacts of these fuels are examined.

INTRODUCTION:

High energy density liquid fuels are the predominant form of energy used for transportation worldwide. The existing infrastructure for production, refining, distribution, and use of liquid fuels represents an enormous investment worldwide, especially so for the Organization of Economic Cooperation and Development (OECD) countries that are transportation rich. The pressures of potential resource limitations for petroleum and the drive toward a cleaner environment have aroused considerable interest in developing alternative fuels for transportation. These alternatives include non-liquid fuels like natural gas and, perhaps in the future, hydrogen. If it is considered to be economically and technically expedient to continue to use the existing liquid fuels infrastructure rather than to change to a gas-based system, liquid fuels could still be produced from non-petroleum sources. The most abundant fossil fuel source worldwide is coal and this can be used to produce high quality liquid fuels. Natural gas can also be used as a source of liquid transportation fuels. Previous studies at MITRE have examined potential world energy supply and demand scenarios till the year 2100⁽¹⁾. These hypothetical scenarios show that total world energy demand increases from the current annual use of 360 exajoules to about 1,100 exajoules by 2100. This projection assumes that energy conversion and end-use efficiency increase such that after 33 years existing equipment is replaced by new equipment that saves 33 percent of the energy. This 33 cycle continues for another two cycles of continuing efficiency improvements saving an additional 16.6 and 8.3 percent respectively. Recoverable oil and gas resources are assumed to be 10,000 exajoules each⁽²⁾, and they will be essentially depleted by 2100. The purpose of this look into the future is to demonstrate that after 2030 oil production will be in decline and an alternative to petroleum-based fuels will have to be found.

Coal as an alternative feedstock for transportation fuels:

The key to converting solid coal to liquid fuel is hydrogen. Liquid fuels typically contain about 14 percent hydrogen whereas coal contains around 5 percent. This hydrogen deficit can be made up by forcing hydrogen into the coal under pressure (so-called direct liquefaction⁽³⁾), or by gasifying the coal with oxygen and steam to a synthesis gas containing hydrogen and carbon monoxide that is then passed over catalysts to form hydrocarbons (so-called indirect liquefaction⁽⁴⁾). For direct liquefaction, coal is slurried with a recycle oil and heated under a high pressure of hydrogen to produce a synthetic crude oil that can be upgraded into specification transport fuels by existing petroleum

refinery processes. The hydrogen is produced by gasification of coal and residue or by natural gas steam reforming. For indirect liquefaction, the synthesis gas produced is passed over Fischer-Tropsch (F-T) catalysts where a series of hydrocarbons ranging from C_1 to about C_{200} are produced. These can also be refined to produce specification liquid fuels by using mild refinery operations.

Direct liquefaction, invented in the early 20th century by Bergius, was used extensively by the Germans in World War II to produce high octane aviation fuel, and since that time research and development have completely transformed the technology. Research sponsored by the United States Department of Energy over the last fifteen years has led to the development of a catalytic two-stage liquefaction process⁽⁵⁾ (CTSL) that uses two high pressure ebullating bed reactors in series to solubilize coal and upgrade it to a distillate raw product containing about 13 percent hydrogen at an overall thermal efficiency of about 66 percent. Liquid distillate yields of over 70 percent on a moisture ash-free (MAF) coal basis are regularly obtained with bituminous coals, and yields of 60 to 65 percent are usually obtained with low rank coals as feedstock. This translates into oil yields of over 3.5 barrels (557 litres) per tonne of MAF coal.

Indirect liquefaction technology is commercialized in South Africa and produces about a third of that country's gasoline and diesel fuel. The South African Synthetic Oil Company (SASOL)⁽⁶⁾ plants produce together over 100,000 barrels per day of fuels. When SASOL made the decision to build these plants the only commercially available coal gasifier that met the requirement of processing high ash South African coals was the Lurgi dry-ash gasifier. Today, however, research and development in coal gasification has resulted in the commercialization of highly efficient entrained gasifiers such as Shell and Texaco. These systems that gasify coal at high temperatures and pressures can process all coals to produce a synthesis gas containing only carbon monoxide and hydrogen. These entrained gasifiers that have net efficiencies for synthesis gas production of about 80 percent greatly improve the overall efficiency, hence the economics, of indirect liquefaction. The other area that has led to significant improvements in the efficiency and economics of indirect liquefaction is the development of advanced F-T synthesis technology. Shell has developed advanced fixed-bed reactor technology for F-T synthesis and is currently operating a plant in Malaysia for the production of diesel fuel and waxes from off-shore natural gas. SASOL has developed an advanced Synthol reactor that uses a fixed fluid bed concept as opposed to the circulating fluid bed currently at use in the SASOL plants. SASOL has also developed a slurry F-T reactor that promises to be even more cost effective. The United States Department of Energy is also funding research aimed at developing both an advanced slurry F-T reactor system and an effective F-T catalyst to use in the advanced reactor. This system being studied both at the bench-scale and at the Alternate Fuels Development Unit at Laporte Texas will be compatible with the synthesis gas produced in the advanced entrained coal gasifiers mentioned above.

In a commercial indirect coal liquefaction facility, the synthesis gas produced in the coal gasifiers is purified and shifted then sent to the F-T reactors where a whole range of hydrocarbons are produced. The unconverted synthesis gas together with methane and ethane is sent to an autothermal reformer where the methane and ethane is converted to hydrogen and carbon monoxide. This is then recycled to the F-T reactors. The hydrocarbon products are separated and the gasoline and diesel boiling range fractions are sent to the downstream refinery to be upgraded to specification fuels. The heavy wax hydrocarbons are hydrocracked to additional gasoline and diesel and also sent to the refinery.

Natural gas as feedstock for production of liquid transportation fuels:

As an alternative to using natural gas in its gaseous state as a transportation fuel, it can be converted to specification gasoline and diesel fuel so that the existing liquid fuels infrastructure can be utilized. This is commercialized in New Zealand where natural gas is converted into methanol and the methanol is converted into gasoline using the Mobil

Methanol-to-Gasoline (MTG) technology⁽⁹⁾. Shell is converting remote natural gas in Malaysia into liquids that can be transported by tanker to market.

For indirect liquefaction, natural gas can be steam reformed or partially oxidized to synthesis gas. This gas is then processed in the same manner as the coal-derived synthesis gas described above. Thus improvements in F-T technology are applicable to natural gas processing. In addition, there have been recent advances in catalytic partial oxidation that can produce lower hydrogen to carbon monoxide synthesis gas at lower cost. For direct liquefaction, natural gas can be used as the source of hydrogen instead of coal, so that coal is only sent to the liquefaction reactors. This results in elimination of the coal gasification plant from the direct plant. In addition, the coal handling units can be reduced in size and the plant electric power required is reduced. Thus, using natural gas for this application lowers capital investment of the direct coal liquefaction plant and, depending on the cost of the natural gas, can result in a lower required selling price of the coal derived transportation fuels. A sensitivity analysis of the equivalent crude price versus natural gas price for this case, where gas is used to produce hydrogen in the direct coal liquefaction plant, shows that using natural gas can result in lower costs for coal liquids up to a natural gas price of about \$4 per million Btu (\$4.22 per GigaJoule). Using natural gas for hydrogen production also has a significant positive impact on the carbon dioxide produced per product barrel. This quantity can be reduced from about 0.42 tonnes per product barrel when coal is used for hydrogen to 0.21 tonnes in the natural gas case.

Economics of fuels production from coal and natural gas:

At the MITRE Corporation, computerized simulation models of coal and natural gas based liquefaction technologies have been developed as part of our funding support from Sandia National Laboratories and the United States Department of Energy^(7,8). In these models, test data from ongoing research and development is used to develop conceptual commercial plants for direct and indirect coal liquefaction, and natural gas based plants. Construction and capital costs of the plants are estimated together with operating costs. Using a constant set of economic parameters the required selling price of liquid fuels can be calculated. This price is then adjusted to an equivalent crude price.

Quality and environmental impact of coal-derived transportation fuels:

Direct coal liquefaction produces an all distillate product that can be refined using conventional hydrotreating, hydrocracking, fluid catalytic cracking, and reforming to yield high octane gasoline, high density jet fuel and 45 cetane diesel. Indirect liquefaction produces a paraffinic gasoline whose octane can be adjusted by reforming or by adding octane enhancers like alcohols or ethers. The diesel fraction is excellent, has a cetane of over 70 and zero aromatics and sulfur. These refined products can exceed current transportation fuel specifications and their use will have a positive effect on air quality. The paraffinic indirect naphtha can be blended with the aromatic direct naphtha to minimize the amount of refining required. Similarly, the aromatic diesel from direct liquefaction can be blended with the paraffinic diesel from indirect. Thus a hybrid plant concept where both direct and indirect technologies are sited at the same location may have considerable merit.

CONCLUSION:

Coal and natural gas can be used as resources to produce specification liquid transportation fuels that make use of the existing liquid fuels refining, distribution and end-use infrastructure. Although the costs of these fuels are higher than current crude prices, they can be competitive with crude oil at about \$30 to \$35 per barrel. The United States Energy Information Agency (EIA)⁽¹⁰⁾ has just published its latest World oil price (WOP) projections. In their reference scenario, the WOP is expected to reach \$35 per barrel by the year 2015.

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DEASHING OF COAL LIQUIDS BY SONICALLY ASSISTED FILTRATION

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INTRODUCTION

This project seeks to improve the effectiveness and reduce the cost of coal liquefaction by novel applications of sonic and ultrasonic energy. The specific purpose of this project is to develop and improve means for the economical removal of dispersed solid particles of ash, unreacted coal, and spent catalyst from direct and indirect coal liquefaction resid by using sonic or ultrasonic waves. Product streams containing solids are generated in both direct and indirect coal liquefaction processes. Direct coal liquefaction processes generate liquid products which contain solids including coal-originated mineral matter, unreacted coal, and spent dispersed catalyst. The removal of these solids from a product stream is one of the most difficult problems in direct coal liquefaction processes. In the existing direct liquefaction processes, the liquefaction reactor(s) effluent is distilled to recover valuable product fractions before the solids are separated from remaining liquids. In consequence, the solids are concentrated in the distillation bottom fractions which are difficult to filter due to their high viscosity. The problem is aggravated by the fact that the solids are predominantly present as micron-sized particles. Removal of solids from coal liquefaction products can be accomplished in several ways. Conventional filtration used in early liquefaction technologies was mechanically troublesome and proved inefficient for processes producing high concentrations of solids in coal liquefaction products of high viscosity, e.g., SRC-I. Efforts were made to improve sedimentation and filtration rates in the deashing of coal liquids through partial precipitation of asphaltenes^{1,2} and using electric fields³. However, no substantial process improvements resulted for the coal liquefaction technology at the time. During the seventies, two other operations for rejecting solids from coal liquefaction product streams were introduced, namely, anti-solvent deashing⁴, implemented by Lummus in a two-stage liquefaction process, and Kerr-McGee's critical solvent deashing⁵ which was employed at the Wilsonville coal liquefaction facility for solids rejection⁶. However, it was reported that up to 30% by weight of the feed could be lost in the rejected stream^{2,7}. At present, Hydrocarbon Research Inc. uses improved filtration of atmospheric distillation resid in a catalytic two-stage direct coal liquefaction process⁸. Other developments⁹ indicate that advanced techniques of solid/liquid separation, e.g., crossflow filtration, could further improve the separation of solids from coal liquefaction products. It also has been suggested¹⁰ that acoustic, electric, and magnetic fields can prevent filter clogging and membrane fouling during crossflow filtration of suspensions. Mechanisms at work include turbulence from cavitation, microstreaming effects and viscosity reduction due to localized heating. Increased filtrate fluxes result from insonation of filtration media during filtration. Crossflow filtration is suitable for continuous flow operation and, when coupled with a sonic or ultrasonic field, may constitute a solution to operational problems of solids separation in coal liquefaction. However, for the efficient and trouble-free operation of crossflow filters the problems arising from dealing with highly viscous coal liquefaction resid need to be avoided. Either crossflow filters suitable for work at elevated temperatures at reduced resid viscosity should be used or the coal liquefaction process network should be modified to allow for dilution of resid using a distillate fraction, e.g., naphtha, diesel oil, etc., to reduce the viscosity of resid. As perhaps even a more practical alternative, field-assisted crossflow filtration of the reactor's effluent stream prior to the distillation step should be considered. Such an approach will circumvent the more difficult separation of fine and ultrafine solids from highly viscous coal liquefaction resid.

EXPERIMENTAL

Liquefaction Resid Characteristics. An atmospheric flashed bottoms stream from Wilsonville Run No. 260 was used in the deashing tests. The V-1067 resid sample (boiling above 850° F, specific gravity 1.24) represents the ashy second-stage product stream which was recycled after partial deashing in the Close-Coupled Integrated Two-Stage Liquefaction process. The resid typically contained 10.1% wt. ash, 30.1% tetrahydrofuran (THF)-insoluble solids, 2.0% THF-soluble and toluene-insoluble preasphaltenes, 21.1% asphaltenes and 46.9% hexane-soluble oil component by weight. The THF-insoluble solids isolated from the resid were analyzed for particle size distribution by wet screening using THF-water mixtures as dispersing liquids. Analyses have shown that the largest particles are about 300 microns in diameter and that 59.5% by weight of the solids are smaller than 5 microns. Based on laser diffraction measurements, it was estimated that 42.9% by weight of the solids is smaller than 1.9 microns in diameter.

Crossflow Filtration Apparatus. A state-of-the-art crossflow filter utilizing 2-micron porosity stainless steel tubes as the filtration medium was built and used in the deashing tests. The crossflow filter was coupled with a 650-watt computer-based variable-frequency sonic transducer to radiate sonic waves inside the crossflow filter directly exposing the filter elements to the sonic field. Figure 1 shows the configuration of the crossflow filter apparatus. Sonic waves were radiated parallel to the filtering surfaces of the crossflow filter. This feature was incorporated in the design of the crossflow filter after earlier, less successful, experiments in which in-situ sonic waves were radiated at a right angle to the filtering surface. In this way, the build-up of solids at the filter medium, often resulting in severe clogging, was eliminated possibly due to the sonically generated rapid movement of fluid parallel to the filtering surface. Detrimental fixing of solid particles in the pores of the filter medium due to the action of high-intensity sound was found to be minimal.

RESULTS AND DISCUSSION

Crossflow Filtration. In this series of tests, the V-1067 resid, diluted with No. 2 fuel oil (1:3 by vol.), was used as the feed. A 5-kHz pulsed sound at 650 watts was used for the insonation according to a preprogrammed sequence of 5 pulses per second. Each pulse was 40-cycles long, i.e., 8 milliseconds. Throughout the duration of filtration, samples of filtrate and of circulated slurry were collected for ash and solids content analyses. The filtrate flow rate was also measured as a function of filtration time. The reference test was performed in exactly the same manner except the sonic transducer was not energized. Table 1 and Figure 2 show the effect of 5-kHz sonic treatment on the filtrate flow rate and filtrate ash content as a function of filtration time. Solids-free and ashless filtrates were obtained in both cases, with and without the sonic energy present during filtration. A clear beneficial effect of sonic waves is evident from the comparison of the filtrate flow rates. In the presence of 5-kHz sonic waves applied in-situ, the filtrate flow rate was greater than that of the reference test by a factor of up to 2.74. Total filtrate volumes collected after 90-minute filtrations were 1.25 and 2.60 liters for the reference and the 5-kHz test, respectively. The increased filtration performance due to in-situ insonation of the crossflow filter is also confirmed by the increased solids and ash contents of the circulated slurry as shown in Table 2 and Figure 3. Based on these unoptimized bench-scale crossflow filtration tests, and assuming the cost of electricity at \$0.07/kwh, the operating cost of sonic treatment was calculated to be 1.70 \$/bbl of filtrate.

Batch Filtrations. Reference Tests. The remaining solids concentrates from continuous cross-flow filtration experiments still contain from 70 to 80% by weight of hexane-soluble oil components. To test further processing options for the solids concentrates, two samples of concentrate containing 77.6% of oil by weight were subjected to conventional batch filtration on Whatman No. 5 filter discs using vacuum at room temperature. Table 3 shows the results of solubility analyses by Soxhlet extraction using n-hexane, toluene, and

THF, for cakes from two parallel batch filtrations, Cake I and Cake II. For comparison, solubility analyses of the as-received V-1067 resid and the solids concentrate are included. The oil and asphaltene contents of the filtration cakes are significantly reduced compared to oil and asphaltene contents of the V-1067 resid, while the percent of THF insolubles and percent preasphaltenes both have increased. Up to 88-hour long filtrations produced ashless filtrates and filtration cakes which appeared dry but still contained approximately 33% by weight of hexane-soluble oil.

Sonically Assisted Batch Filtrations. Three batch filtrations of the solids concentrate were conducted at room temperature. Whatman No. 5 filter paper was used as the filter medium. A brief description of the test procedure is as follows. A well stirred sample of the solids concentrate was placed in a filtration funnel and the excess fuel oil was filtered out by applying vacuum. As soon as air broke through the filter cake, a 20-kHz sonic probe was placed in contact with the cake and energized at 250 watts using a pulsed mode of operation at 80% duty cycle. Throughout the entire time of insonation, the probe was slightly pressed against the surface of the filter cake to ensure a good contact of probe with the surface of the cake. The cake rapidly liquified in the presence of sonic energy resulting in an additional amount of oil passing through the filter and a dry and compact cake. The oil filtrate was found to contain no solids or ash. During the insonation, the filtration cakes released a significant amount of oil vapors and possibly products of a decomposition reaction. Cake temperatures as high as 170 °C were measured at the cake surface immediately after completion of insonations. It is worth noting that these high temperature increases of diluted V-1067 resid did not occur in earlier tests with liquid suspensions of V-1067 in No. 2 fuel oil, despite an intense acoustic cavitation taking place within the suspension. Possibly, the solids loading of the suspension must be above a certain threshold for efficient absorption of sonic energy. For a V-1067 resid and No. 2 fuel oil mixture, this solids loading threshold is at about 50% solids by weight.

Table 3 shows the solubility analyses of filtration cakes; cake 3 through 5 were insonated for 5, 10, and 20 minutes. As the insonation time increased the oil content of the filtration cake decreased while the THF insolubles and preasphaltenes contents both increased. It is evident that more oil can be recovered from solids concentrates by using sonic energy. The effect of insonation on the rate of filtration is dramatic. The analysis of the filtration cake insonated for only 10 minutes showed an oil content of 24.3% while the 88-hour reference tests without insonation produced cakes containing 32.0 and 33.5% of oil by weight. This corresponds to an over 600-fold increase in the average filtration rate. Little further improvement in the quality of the filtered solids was achieved by prolonging the insonation to 20 minutes.

ACKNOWLEDGEMENTS

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**Table 1. Sonically Enhanced Filtration of V-1067 Coal Liquefaction Resid.
Filtration Rates and Filtrate Ash Contents.**

| Filtration Time (min.) | REFERENCE | | 5-kHz SOUND | | FLOW RATE RATIO |
|------------------------------|------------------------|------------------|------------------------|------------------|--------------------|
| | Flow Rate (ml/min.) | % Ash (% wt.) | Flow Rate (ml/min.) | % Ash (% wt.) | |
| 2 | 80.0 | - | 83.0 | - | 1.04 |
| 5 | - | - | 45.8 | - | - |
| 7 | 42.9 | - | - | - | - |
| 9 | 31.2 | - | - | - | - |
| 10 | - | 0.000 | 39.5 | 0.000 | - |
| 15 | 18.1 | 0.000 | - | 0.000 | - |
| 20 | - | - | 35.7 | - | - |
| 25 | 14.3 | - | - | - | - |
| 30 | 13.9 | 0.000 | 31.2 | 0.000 | 2.24 |
| 40 | 10.3 | - | 23.4 | - | 2.27 |
| 60 | 8.7 | 0.000 | 20.5 | 0.000 | 2.36 |
| 90 | 7.3 | 0.000 | 20.0 | 0.000 | 2.74 |

**Table 2. Sonically Enhanced Filtration of V-1067 Coal Liquefaction Resid.
Slurry Ash and Solids Contents (n-Hexane Insoluble Matter).**

| Filtration Time (min.) | REFERENCE | | 5-kHz SOUND | | FLOW RATE RATIO |
|------------------------------|---------------------|------------------|---------------------|------------------|--------------------|
| | % Solids (% wt.) | % Ash (% wt.) | % Solids (% wt.) | % Ash (% wt.) | |
| 0 | 8.24 | 1.55 | 8.14 | 1.58 | 0.98 |
| 10 | 7.32 | - | 8.61 | - | 1.18 |
| 20 | 7.46 | - | 10.22 | - | 1.37 |
| 30 | 7.96 | - | 12.20 | - | 1.53 |
| 40 | 12.78 | - | - | - | - |
| 60 | - | 1.74 | 15.77 | 1.87 | - |
| 90 | 15.32 | 1.77 | 17.32 | 1.93 | 1.13 |

**Table 3. Solubility Analysis of Filter Cakes From Batch Filtrations of
Solids Concentrate.**

| Weight Percent | | | | | | | |
|-------------------------|--------|-------|--------|--------|--------|---------|---------|
| | V-1067 | Conc. | Cake 1 | Cake 2 | Cake 3 | Cake 4 | Cake 5 |
| Insonation time: | - | - | 0 min. | 0 min. | 5 min. | 10 min. | 20 min. |
| Filtration time: | - | - | 88 hrs | 88 hrs | 5 min. | 10 min. | 20 min. |
| <u>Solubility Class</u> | | | | | | | |
| Oil | 46.9 | 77.6 | 33.5 | 32.0 | 36.9 | 24.3 | 24.1 |
| Asphaltenes | 21.1 | 7.2 | 13.8 | 14.6 | 14.2 | 15.5 | 15.5 |
| Preasphaltenes | 4.3 | 3.4 | 17.9 | 17.6 | 17.5 | 22.0 | 22.1 |
| THF Insolubles | 27.7 | 11.8 | 34.8 | 35.0 | 31.4 | 38.2 | 38.2 |
| | 100.0 | 99.1 | 100.0 | 99.2 | 100.0 | 100.0 | 99.9 |

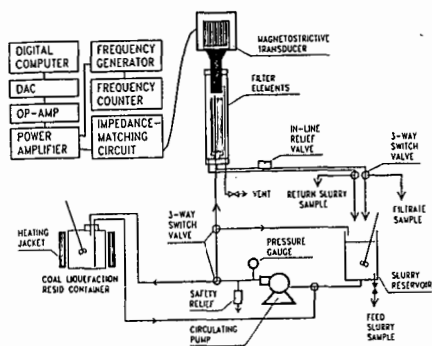


Figure 1. Configuration of the crossflow filtration apparatus.

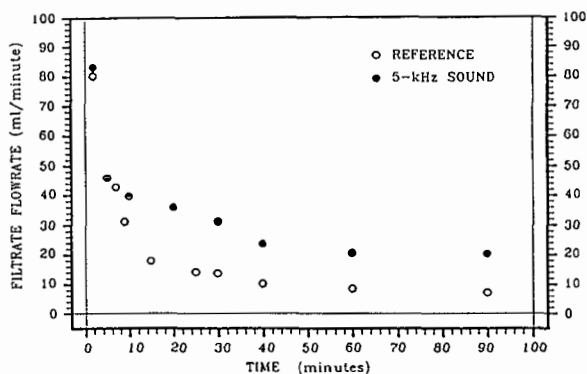


Figure 2. Effect of sonic waves on filtrate flow rates.

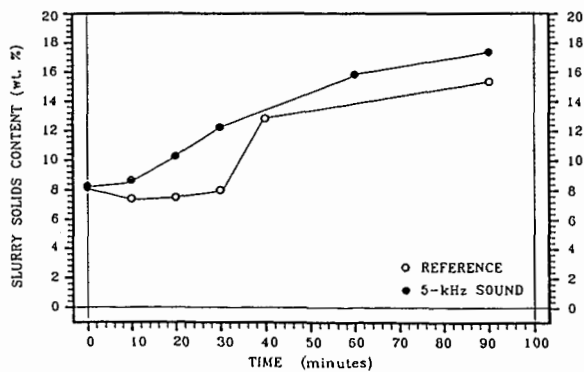


Figure 3. Effect of sonic waves on slurry solids content.

PETC's ON-SITE NATURAL GAS CONVERSION EFFORTS

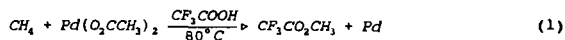
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KEYWORDS Methane, Oxyhydrochlorination, Organometallic Reactions

ABSTRACT Investigation of the direct conversion of natural gas (i.e., methane) to transportation fuels has been an ongoing effort at PETC for over 10 years. Two of our recent areas of interest have been the oxyhydrochlorination (OHC) of methane and the oxidation of methane by organometallics. The OHC reaction is a two-step process in which methane, hydrogen chloride, and oxygen are reacted to produce methyl chloride. The methyl chloride is then reacted over a zeolite to produce gasoline-range hydrocarbons. Another area of interest, the oxidation of methane with organometallics, has produced interesting results. The reported reaction occurs between methane (at 800 psig, 5.52 MPa) and palladium(II) acetate in trifluoroacetic acid at 80°C. The product, methyl trifluoroacetate, is readily hydrolyzed to produce methanol and trifluoroacetic acid.

INTRODUCTION A significant portion of proven global natural gas reserves are in remote areas of the world where transporting the gas to market is not economically feasible. The conversion of natural gas to liquid fuels would permit facile storage, transportation, and distribution of a higher energy density fuel using established technologies and distribution networks. Key to a natural gas conversion process is the conversion of methane, the major component. The Pittsburgh Energy Technology Center (PETC) has been involved in this effort. Recent research has led to a two-step process for the conversion of methane to gasoline-range hydrocarbons¹⁻⁴. Methane, oxygen, and hydrogen chloride react over an oxyhydrochlorination (OHC) catalyst in the first step to produce predominantly chloromethane and water. In the second step, the chloromethane is catalytically converted to higher hydrocarbons, mainly in the gasoline (C₄-C₁₀) boiling range, by a pentasil-type zeolite such as ZSM-5.

Reports have appeared in the literature describing the use of organometallic complexes to selectively oxidize methane.^{5,6} Investigation of one of these reaction schemes in our laboratory has produced interesting results.⁷⁻⁹ Our research effort was an extension of work reported by Sen and coworkers.⁷⁻⁹ The reported reaction occurs between methane (at 800 psig 5.52 MPa) and palladium(II) acetate in trifluoroacetic acid at 80°C (Equation 1). The product, methyl trifluoroacetate, is readily hydrolyzed to produce methanol and trifluoroacetic acid.



OHC REACTIONS:

EXPERIMENTAL The catalysts for the OHC reaction were prepared by sequential deposition of the appropriate metal chlorides, or their precursors, in non-aqueous solvents onto a fumed silica support. The catalysts were tested for OHC activity under a predetermined set of conditions and compared to the copper/potassium/lanthanum chloride catalyst. All reactions were conducted in a 0.5-in (1.27-cm) o.d. x 7-in (17.8-cm) quartz up-flow reactor tube. A blank catalyst was prepared under identical conditions to those used for the metals but only containing potassium and lanthanum chlorides on the silica support. The catalysts were activated in a stream of hydrogen chloride at 300°C prior to testing. Composition of the catalysts, by weight, is given in Table I. An on-line mass spectrometer was used to determine conversions and product yield.

RESULTS AND DISCUSSION Table II lists reactant conversions under conditions utilized for the copper/potassium/lanthanum chloride catalyst and Table III lists the normalized carbon product distribution. With the exception of the cobalt catalyst, all catalysts exhibited a lower conversion of methane and lower methyl chloride production than did the copper. Temperature profiles for all the catalysts were performed along with lifetime studies for the copper and cobalt catalysts. Reactant conversion and product distribution remained constant during the 400 hours on stream for both the copper and cobalt catalysts.

Differences in activity of the copper and cobalt OHC catalysts have been observed depending on the person in our laboratory who prepared them. The lower activity catalysts result in both lower conversions and poorer selectivity for chloromethane. In an effort to better understand these observations, the catalysts were analyzed for structural differences.

Preliminary scanning electron microscopic (SEM) examination of two supported copper OHC catalyst samples showed some differences in morphology and segregation of Cu, Cl, La, and K. The overall elemental compositions of the two samples were similar, as shown in the energy dispersive spectroscopy (EDS) spectra, however, the SEM micrographs displayed a difference in particle size. The more active catalyst exhibited a finer particle texture with fewer large copper-potassium chloride needles. Identical results were observed for two samples of the Co-OHC catalyst that exhibited different OHC activities.

X-ray diffraction (XRD) studies performed on the two Cu-OHC catalyst samples utilizing a Cu-K_α radiation exhibited some differences. The most significant

was at 2 θ angles of 11.6 and 6.05 degrees. The more active catalyst exhibited intensities at these positions which were greater by a factor of 2 and 5, respectively. Upon exposure of the catalyst sample to humid air the 2 θ peak at 6.05 degrees disappeared.

CHLOROMETHANE CONVERSION REACTIONS:

EXPERIMENTAL All reactions were conducted in a 0.5-in (1.27-cm) o.d. x 7-in (17.8-cm) quartz up-flow reactor tube. The ZSM-5 was obtained from Mobil Oil Corporation in the ammonium form with a silica-to-alumina ratio of 70:1. The ammonium form was converted to the acid form by calcining in air at 538°C for 16 hours. Typically, 1.0 g of ZSM-5 zeolite was supported on a deactivated quartz-wool plug, heated to 350°C, and exposed to methyl chloride or mixtures of chloromethanes approximating the composition produced in the OHC reaction. Flows of reactants were selected to maintain a weight hourly space velocity (WHSV) of 1. An on-line mass spectrometer was used to determine conversion.

The liquid condensate was collected in an ice bath during the experiments and was analyzed by utilizing a 100 m X 0.25 mm i.d. fused silica column coated with a 0.5 μ m film of 100% methylpolysiloxane (Petrocol DH) and a helium carrier gas having an average linear velocity of 31 cm per second at 30°C. The low boiling, low molecular weight products not condensed in the ice bath were determined by directly sampling the reactor effluent product vapor and analyzing it by gas chromatography using a 50 meter X 0.32 mm porous layer open tubular (PLOT) column containing Al₂O₃/KCl¹⁰. The identifications made in this manner were confirmed by combined GC-MS and/or GC-FTIR. GC-MS was performed using a Hewlett-Packard 5988A system equipped and operated with the same chromatographic column and conditions as above. Further confirmation of these identifications was obtained by combined GC-FTIR using a Digilab FTS 65 GC/C 32 system equipped with a Hewlett-Packard 5880 GC and the same column mentioned above utilizing identical chromatographic conditions. The GC-FTIR experiments were performed at Digilab in Cambridge, Massachusetts.

RESULTS AND DISCUSSION In a typical experiment, chloromethane conversion varies from 98.5% to 100%. Over 240 compounds have been analytically separated in the reaction mixture and individual compounds constituting about 90 weight percent of the products have been identified. The liquid condensate did not contain significant amounts of the low boiling, low molecular weight products formed during the reaction. These compounds were determined in a separate experiment by sampling the reactor effluent immediately after exiting the reactor and analyzing them by using on-line gas chromatography employing an alumina PLOT column.

At 360°C, 1,2,4-trimethylbenzene is a major organic product formed in the reaction and constitutes about 45 weight percent of the total liquid product. Tetra- and pentamethylbenzenes are also found in the product but in substantially lower amounts.

A few weight percent (~1%) of the products were identified to contain chlorine. A large portion of these are 2-chloroalkanes. These are postulated to be formed by Markovnikov addition of hydrogen chloride, an elimination product of chloromethane conversion, to terminal olefins. The addition may occur in the reactor or down stream of the reactor in a hot zone.

ORGANOMETALLIC METHANE REACTIONS:

EXPERIMENTAL All reactions were conducted in a sealed, 0.5-in (1.27-cm) o.d. x 12-in (30.5-cm) silica-lined stainless-steel batch reactor. The reactor was lined by Restek, Inc. Total volume of the reactor system was <35 mL. In order to reproduce the literature results, experimental conditions were the same as those reported by Sen and coworkers.⁷

The reactor was rinsed with 5.0 g (3.3 mL) of dry trifluoroacetic acid, dried in a vacuum oven at 110°C, backfilled with dry nitrogen, and charged with reactants. Typically, the charge consisted of 0.15 g of palladium(II) acetate dissolved in 5.00 g of trifluoroacetic acid. After being connected to the gas manifold, the reactor was purged several times with helium at 1000 psig (6.89 MPa), followed by several purges of methane with a final methane pressure of 800 psig (5.52 MPa), and isolated from the gas manifold.

When ¹³CH₄ was used, the reactor was immersed in a liquid nitrogen bath after being purged with helium. When the temperature had reached -190°C, the reactor was connected to a mechanical vacuum pump and evacuated. The reactor was then isolated from the vacuum pump and, while still immersed in liquid nitrogen, was connected to the cylinders of ¹³CH₄ to allow transfer of the cylinders' contents to the reactor. After transfer of the cylinder's contents, the reactor was sealed and placed in a silicone oil bath. The ¹³CH₄, specified by the supplier at 99% isotopic purity, was supplied in 1-L cylinders at 20 psig (0.14 MPa) pressure. The contents of two cylinders were required to obtain the necessary >800 psig (5.52 MPa) pressure for reaction.

When necessary, the gases were dried prior to entering the reactor by passing through an 8-ft (2.44-m) x 1/4-in (0.64-cm) coil of stainless-steel tubing immersed in an acetone/dry ice bath.

The reactor was heated in a bath of silicone oil at 80°C for 5 days. The reactor pressure was monitored by a pressure transducer and recorded during the run. Blank runs followed the same procedure with the exception of helium replacing methane.

Upon completion of the run, the reactor was depressurized and the liquid was removed for analysis. After removal of the reactor's liquid contents, the reactor was filled with deionized water, capped, and placed in a 720-W ultrasonic cleaner for one hour. This procedure loosened the palladium metal

which formed during the reaction. The solution was then passed through a preweighed 0.50- μ m Teflon[®] filter and air dried. The residue on the filter was removed and identified by SEM and EDS. Gaseous components were analyzed on a Hewlett-Packard 5730 gas chromatograph. Liquid samples were analyzed on a Hewlett-Packard 5988A GC/MS system.

RESULTS AND DISCUSSION The results reported by Sen and coworkers were reproduced (Run 241); production of methyl trifluoroacetate was observed and a fine metallic powder was recovered. SEM and EDS analysis of the powder confirmed it to be palladium metal with crystallites of the order of 1 μ m in size. Quantitative analysis of the palladium metal residue indicated >80% of the palladium acetate was recovered as palladium metal. Methane conversion, calculated by the difference in pressure from the beginning to the end of the run, was ~3 mol% (Table IV). Analysis of the reaction mixture from Run 241 identified several other oxygenated compounds and water. To determine the source of these compounds, the palladium(II) acetate dissolved in trifluoroacetic acid for Run 242 was analyzed prior to introduction of methane. This revealed the presence of methyl trifluoroacetate, the product of methane oxidation, prior to introduction of methane, and the same components identified before.

The trifluoroacetic acid was analyzed to determine if the methyl trifluoroacetate and other compounds found in Runs 241 and 242 were present. All the unexpected compounds except methyl trifluoroacetate were detected, including a significant quantity of water. A blank run was conducted in which the methane was replaced with helium at 800 psig (5.52 MPa). All reaction conditions and operations were identical to previous runs. This experiment resulted in the production of methyl trifluoroacetate and a 68.30% recovery of palladium metal. The only logical origin of the methyl group of the ester is via decomposition of the acetate ligand of the starting material.

The gas in the reactor was sampled prior to venting and recovery of liquid products. Analysis of the gas samples by high-resolution gas chromatography, after completion of the experiments, showed only the components present in the feed gas.

For use in the remaining experiments, dry, high-purity trifluoroacetic acid was obtained in sealed ampules containing enough acid for a single use. Analysis of this trifluoroacetic acid revealed no detectable quantities of water or other impurities previously detected. The blank run was repeated. After 150 hours at 80°C and 800 psig (5.52 MPa) helium, the reactor was opened and the solution removed for analysis and comparison with the starting material. No difference in composition was detected between the two samples. Water (8 x 10⁻³ moles, a 10 fold excess) was then added to the mixture of Run 244, the reactor was charged with helium at 800 psig (5.52 MPa), and held at 80°C for 150 hours. Analysis of the products of reaction (Run 245) revealed the presence of methyl trifluoroacetate and methyl acetate. Since no methane was present in the system, the only source of the methyl group in the products is from the displaced acetate. This observation is inconsistent with that of Sen⁹ in that he did not observe any deuterium incorporation into the methyl trifluoroacetate when Pd(O₂CCD₃)₂ was used.

The first experiment (Run 246) to use both methane and the dry, high purity trifluoroacetic acid resulted in products similar to previous experiments with the exception that the amount of palladium metal recovered was only 39.20 mol%, a reduction of >50%. We attribute this decrease to the absence of side reactions caused by the water in the trifluoroacetic acid.

To determine if any methane from the gas phase was involved in the reaction, an experiment (Run 248) was conducted using methane that was isotopically enriched in carbon-13. Oxidation products arising solely from the labelled methane, determined by GC-MS, would eliminate the possibility of products arising from the acetate ligand on the palladium(II) acetate. The reactor was filled as described above. Operating under conditions similar to previous experiments resulted in similar methane conversions but a recovered palladium metal amount of only 7.88 mol%. Analysis of the product mixture revealed both CF₃C(O)O¹³CH₃ and CF₃C(O)OCH₃. Single Ion Monitoring (SIM) analysis of the isotopic ratio of the labeled products gave a ¹³C/¹²C ratio of 4.98. The composition of the labeled methane was determined by mass spectroscopy to be 93.5% ¹³CH₄ and 6.5% ¹²CH₄, a ratio of 14.38. This means that ~1% of the methyl carbon in the methyl trifluoroacetate comes from a source other than the labeled methane. This confirms our postulate that not all of the product arises from the methane introduced as a reactant.

To test the postulate that the presence of water in the reactor system was responsible for the observed decrease in palladium metal recovery, three experiments were conducted (Runs 250, 252, and 254) in which the gases were dried prior to entering the reactor as described above. The reactor was prepared as in the ¹³CH₄ experiment. After warming to room temperature, 4.8 x 10⁻³ g (2.7 x 10⁻⁴ moles) of water was recovered from the drying trap. The result of these experiments is that the methane consumption and product distribution remained the same as previously observed, but recovery of palladium metal was only 4.21, 7.46, and 8.29 mol%, respectively. This suggests that the presence of water in either the reactants or in the reactor system is responsible for the greater quantities of palladium metal reported in the literature. Water was not detected in the product mixture by GC/MS for these experiments. Quantitation of reaction products for Run 254 revealed that 0.13 weight percent of the product is methyl trifluoroacetate. This corresponds to a conversion of reactants to the desired product of 0.8%.

Sen and coworkers postulated that the mechanism of this reaction is electrophilic attack on the methane by Pd(II), followed by reductive elimination to give Pd metal and the alcohol derivative. This mechanism is supported only by

the fact that palladium is a strong electrophile and a good two electron oxidant. Our observations do not support the original assumption that the reaction, as stated in Equation 1, is a 1:1 stoichiometric reaction between methane and palladium(II) trifluoroacetate. Table IV lists the molar balance for the experiments. The sixth column of the table shows the ratio of methane consumed to palladium metal recovered. The data from the early experiments, when water was present, show that the molar ratio of methane consumed to palladium metal recovered is of the order of 10. In later experiments, when water was removed from the reactants, this ratio is an order of magnitude larger.

These inconsistencies leave open the important questions about the reaction mechanism which is key to proper evaluation of this reaction as a method for direct oxidation of methane. If the methane is being consumed by some other reaction not involving palladium, is the palladium(0) being reoxidized to a palladium(II) complex, or are other impurities present in the system?

CONCLUSION

This brief study may lead to the conclusion that ample opportunity exists to improve the OHC catalyst used in the first step of the PETC Methane-to-Higher Hydrocarbon Process and, accordingly, improve the entire process. Due to regulations limiting the aromatic and chlorine content of gasoline, the chloromethane conversion reaction will need to be fine tuned before commercial consideration. Chloromethane, a high-valued intermediate, may be the choice of product in this reaction scheme.

The study involving organometallics has shown that the reaction expressed in Equation 1 does occur, as confirmed by the production of $\text{CF}_3\text{CO}_2^{13}\text{CH}_3$ from $^{13}\text{CH}_4$, but that this reaction is not responsible for all product methyl trifluoroacetate. When a blank experiment was performed using the highest purity starting materials and replacing methane with helium, methyl trifluoroacetate was detected in the product if water was not excluded from the system. The presence of water in the reaction mixture appears to cause the palladium acetate/trifluoroacetate complex to decompose and produce methyl trifluoroacetate and account for the high yields of palladium metal reported in the literature.

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DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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TABLE I CONSTITUENTS BY WEIGHT

| CATALYST | % METAL CHLORIDE | % SiO_2 | % KCl | % LaCl_3 |
|----------|---------------------|------------------|-------|-------------------|
| Cu | 41.66 | 37.50 | 11.46 | 9.38 |
| Co | 55.17 | 28.82 | 8.81 | 7.20 |
| Ni | 58.46 | 26.70 | 8.16 | 6.68 |
| Pb | 66.96 | 21.24 | 6.49 | 5.31 |
| Ag | 44.73 | 35.53 | 10.86 | 8.88 |
| Pt | 41.66 | 37.50 | 11.46 | 9.38 |
| Cr | 56.24 | 28.12 | 8.61 | 7.03 |
| Blank | 00.00 | 64.29 | 19.64 | 16.07 |

TABLE II REACTANT CONVERSION
3.0 GRAMS CATALYST, RESIDENCE TIME 8.3 SECONDS, TEMP. 340°C,
FLOWS CH₄ = HCl = 4.0 mL/MIN, O₂ = N₂ = 2.0 mL/MIN

| CATALYST | % CH ₄ CONV. | % HCl CONV. | % O ₂ CONV. |
|-----------------|-------------------------|-------------|------------------------|
| Cu | 47.69 | 80.08 | 83.86 |
| Co | 61.03 | 52.54 | 85.48 |
| Ni | 19.31 | 19.81 | 11.11 |
| Pb | 5.51 | 14.86 | 9.41 |
| Ag | 4.54 | 7.95 | 14.03 |
| Pt ^a | 54.34 | 0.01 | 3.10 |
| Pt ^b | 7.36 | 3.29 | 6.56 |
| Cr | 13.15 | 3.54 | 33.21 |
| Blank | 16.16 | 6.63 | 25.31 |

^aAfter 24 hours on stream

^bAfter 48 hours on stream

TABLE III NORMALIZED CARBON PRODUCT DISTRIBUTION
3.0 GRAMS CATALYST, RESIDENCE TIME 8.3 SECONDS, TEMP. 340°C,
FLOWS CH₄ = HCl = 4.0 mL/MIN, O₂ = N₂ = 2.0 mL/MIN

| CATALYST | CH ₃ Cl | CH ₂ Cl ₂ | CHCl ₃ | CCl ₄ | CO | CO ₂ | HCOOH |
|-----------------|--------------------|---------------------------------|-------------------|------------------|-------|-----------------|-------|
| Cu | 30.03 | 39.42 | 9.39 | 0.14 | 0.00 | 12.44 | 8.58 |
| Co | 44.31 | 12.44 | 1.32 | 1.32 | 0.00 | 3.67 | 38.26 |
| Ni | 23.03 | 3.78 | 0.00 | 0.00 | 0.00 | 0.00 | 73.19 |
| Pb | 20.97 | 3.49 | 0.37 | 0.37 | 0.00 | 0.00 | 75.17 |
| Ag | 12.71 | 1.37 | 0.09 | 0.09 | 0.00 | 14.52 | 71.31 |
| Pt ^a | 31.26 | 3.49 | 0.30 | 0.18 | 0.00 | 17.35 | 47.42 |
| Pt ^b | 28.96 | 3.28 | 0.42 | 0.14 | 0.00 | 10.75 | 56.45 |
| Cr | 10.92 | 2.66 | 0.60 | 0.00 | 64.77 | 21.05 | 0.00 |
| Blank | 10.01 | 0.45 | 0.09 | 0.00 | 69.55 | 7.02 | 12.78 |

^aAfter 24 hours on stream

^bAfter 48 hours on stream

TABLE IV ORGANOMETALLIC METHANE OXIDATION RESULTS

| RUN | MOL % Pd METAL FORMED | MOL % CH ₄ CONSUMED | MOLES Pd METAL FORMED (X10 ⁴) | MOLES CH ₄ CONSUMED (X10 ³) | MOLES CH ₄ MOLES Pd | % CH ₄ CONVERTED TO CF ₃ C(O)OCH ₃ |
|-----|-----------------------|--------------------------------|---|--|--------------------------------|---|
| 241 | 83.50 | 3.00 | 4.70 | 4.69 | 9.98 | |
| 242 | 77.00 | 3.13 | 5.14 | 3.59 | 6.99 | |
| 243 | 68.30 | N/A | 4.30 | 0.00 | N/A | |
| 244 | 0.00 | N/A | 0.00 | N/A | N/A | |
| 245 | 83.20 | N/A | 5.76 | 0.00 | N/A | |
| 246 | 39.20 | 6.42 | 2.72 | 4.54 | 16.72 | 0.4 |
| 248 | 7.88 | 4.08 | 0.55 | 3.07 | 56.32 | |
| 250 | 4.21 | 4.01 | 0.29 | 5.94 | 203.84 | |
| 252 | 7.46 | 10.30 | 0.49 | 6.90 | 141.15 | |
| 254 | 8.29 | 9.87 | 0.55 | 8.44 | 153.45 | 0.8 |